The Water Quality Status of Serpent Harbour North Channel 1975

Ministry of the Environment

The Honourable
George A. Kerr, Q.C.,
Minister

K.H. Sharpe,
Deputy Minister

A Project Report

on

"The Water Quality Status of
Serpent Harbour, North Channel 1975"

Submitted in fulfillment of
ULRG Project Report. No. D-28

Prepared By

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SUMMARY

This summary highlights the findings of water quality studies undertaken in Serpent Harbour during 1975, and the trends in materials input to the harbour from Serpent River and Pronto ditch for the period 1967 to 1974.

1) Serpent River accounts for $\sim$ 98% of the ^{226}Ra input to the harbour from all known sources and within any year $\sim$ 50% of the annual ^{226}Ra loading entering the harbour occurs during the months of April, May and June, the period of greatest river discharge. The overall levels of ^{226}Ra entering Serpent Harbour have decreased since the late 1960's. The reduction in radium levels and loadings entering the harbour is attributed to a decrease in mining activity, re-use of process waters at upstream uranium mines, elimination of direct discharges to receiving waters, natural decreases in streamflows and the use of barium chloride treatment. During two 1975 surveys, ^{226}Ra levels >3pCi/l the Ontario Ministry of Environment criterion for surface water supply were noted within Serpent Harbour. On May 30, ^{226}Ra levels >3pCi/l were confined to an area extending $\sim$ 5 km from the river mouth. During the September 23 survey ^{226}Ra levels in excess of the criterion were noted for an area extending $\sim$ 2.7 km from the river mouth. Sediment core and grab sampling undertaken during 1975 indicated near-surface ^{226}Ra accumulations with maximum levels occuring along the southern edge of the harbour. Sediment data indicated recent accumulation and identified the Serpent River as the major source of ^{226}Ra contamination sediment.

2) Serpent Harbour receives loadings of sulphate as a result of upstream mining activity. Sulphate levels measured within the harbour during 1975 were within the OMOE desirable criterion of 50 mg SO_4/ℓ for public water supply.

3) Serpent Harbour receives significant loadings of nitrogenous compounds as a result of upstream mining activity. The largest proportion of the nitrogen load reaching the harbour is primarily in the form of nitrate. The horizontal trends of nitrogen compounds lakeward from Serpent River mouth during the 1975 survey indicated steep diminishing gradients. Ammonia concentrations throughout Serpent Harbour during the 1975 study consistently averaged > .01 mg/l the OMOE desireable criterion for municipal water supply at all stations and extending approximately 10 km from the river mouth.

4) The phosphorus loading to Serpent Harbour is of a minor nature with the bulk of phosphorus being derived from natural land drainage. The horizontal distribution of total and dissolved phosphorus in Serpent Harbour during the 1975 study indicated lower concentrations in the harbour than in the adjacent waters in the North Channel.

5) Although a long term data base for chlorophyll a and phytoplankton abundance does not exist, it is likely that Serpent Harbour could be classified as a potential nutrient enrichment problem area. This consideration is based upon present high nitrogen loadings from the Serpent River, the configuration of the harbour, 1975 chlorophyll a levels and the presence of moderately high heterotrophic bacteria populations. Phosphorus appears to be the limiting factor governing aquatic plant growth in the harbour.

6) Acid mine drainage has been an ongoing problem in the Serpent River drainage basin since the development of the uranium mining industry in the Elliot Lake area. Presently, lime is being used for pH regulation at active and non-active tailings areas. Field alkalinity levels during the 1975 Serpent Harbour study were below the OMOE criterion for the protection of the carbonate buffering system (< 20 mg $CaCO_3$/l) for an area extending approximately 5 km from the river mouth. For the same period, in-situ pH levels within the harbour were within acceptable limits (6.5 to 8.5).

7) Studies in 1975 did not indicate any water quality problems associated with dissolved oxygen, chlorides, conductivity, transparency (Secchi depth and turbidity) and the health oriented indicator bacteria (total coliforms, fecal coliforms and fecal streptococci).

8) Heavy metal analysis of Serpent Harbour waters during 1975 showed no significant differences in the horizontal distribution of total chromium, total cadmium, total lead, total zinc, total nickel and total cobalt. In most cases all reported levels were at or near the detection limit of the analytical method. Total iron was detected above the detection limit; however, levels were well within OMOE permissible criterion for public surface water supply (.3 mgFe/l (1)).

9) The levels of total mercury, total chromium, total cadmium, total copper and total iron in Serpent Harbour surficial sediments were not significantly different from the levels reported for the nearshore surficial sediments of the North Channel. Total lead, total zinc and total nickel levels in the surficial sediments of Serpent Harbour were greater than those reported in North Channel nearshore sediments. The local accumu-

lation of lead, zinc and nickel in harbour sediments may be due to the mineralogy of Serpent River drainage basin. Studies to assess the environmental impact and/or public health significance of heavy metals and radionuclides in sediment were not undertaken during the 1975 survey.

10) The sediments of Serpent Harbour were devoid of detectable quantities of lindane, heptachlor, aldrin, dieldrin, endrin, heptachlor epoxide, PCB's and chlordane. DDE was detected in trace quantities at 14 harbour stations and DDD at two stations.

RECOMMENDATIONS

The following recommendations are forwarded on the basis of existing water quality problems in Serpent Harbour.

Pollution Abatement

1) This report is confined to an evaluation of water quality in Serpent Harbour; however, since water quality problems are related to upstream sources it supports recommendations made in two earlier reports (3,4). Implementation of these earlier recommendations made for the protection of water quality and biota of the river itself should in turn correct the problems found in the harbour.

Surveillance

2) It is recommended that the proposed radioactivity surveillance plan as outlined in Appendix D of the 4th annual report of the Water Quality Board, International Joint Commission be implemented as soon as the interim radioactivity water quality objective is ratified by the Canadian and U. S. federal governments.

INTRODUCTION

In 1973, as part of Upper Lakes Reference Group (ULRG) studies, Serpent Harbour was identified as a potential water quality problem area. Since 1973, a water quality study (ULRG project D-28) was completed in the vicinity of Serpent River mouth. The objective of this study was to determine the extent of water quality impairment, if any, off the mouth of the Serpent River an area where substantial uranium mining activity takes place.

DESCRIPTION OF THE STUDY AREA

Figure 1 shows the location of Serpent River watershed and river mouth relative to Lake Huron and North Channel. Serpent Harbour is located 139km east of the City of Sault Ste. Marie, Ontario and 130 km west-southwest of the City of Sudbury, Ontario.

Serpent Harbour, formed between Murray Fault and an outcrop of Cutler granite (4) extends east-west for 5 km and ranges in width from 0.6 to 1 km. The area from the Serpent River mouth west to Fournier Island encompasses about 4.14 km^2. The harbour has several small islands and drying rocks. Nobles Island is the main feature in the harbour (figure 2) rising 44.2 m above chart datum. Bathymetric contours of the harbour at 3 m intervals are shown in figure 2. The depth, length, shape, slope and orientation of Serpent Harbour are primary factors governing the dispersion of materials input from the Serpent River.

Hydrology and Drainage Basin Characteristics

The Serpent River drainage basin encompasses an area of 1347 km^2 and discharges to the North Channel of Lake Huron. A large portion ($\sim$ 20%) of the total drainage basin area is surface water, mainly accounted for by the great number of small lakes. The largest lake is Quirke, which has a surface area of 18.6 km^2 and a maximum depth of 102 m. Several small uncontrolled dams have been built by the mining companies to provide settling areas for mine tailings; however, these are believed to have very little affect on the flow regime of the Serpent River.

Figure 3 shows a statistical summary of monthly discharge records at Serpent River gauge (Hwy. #17, 8.4 km upstream of Serpent River Mouth) for the period 1966 to 1974. Flows for the period of record ranged from a minimum of 1.4×10^5 m^3/d to a maximum of 77.2×10^5 m^3/d.

Peak discharges during the month of April, May and occasionally June, correlate with periods of snowmelt (figure 3). Discharge during the month of June is probably attributed to the time lag between the snowmelt and upstream lake retention time. River discharges for the month of January, February, July, August and September are reflected in preci-

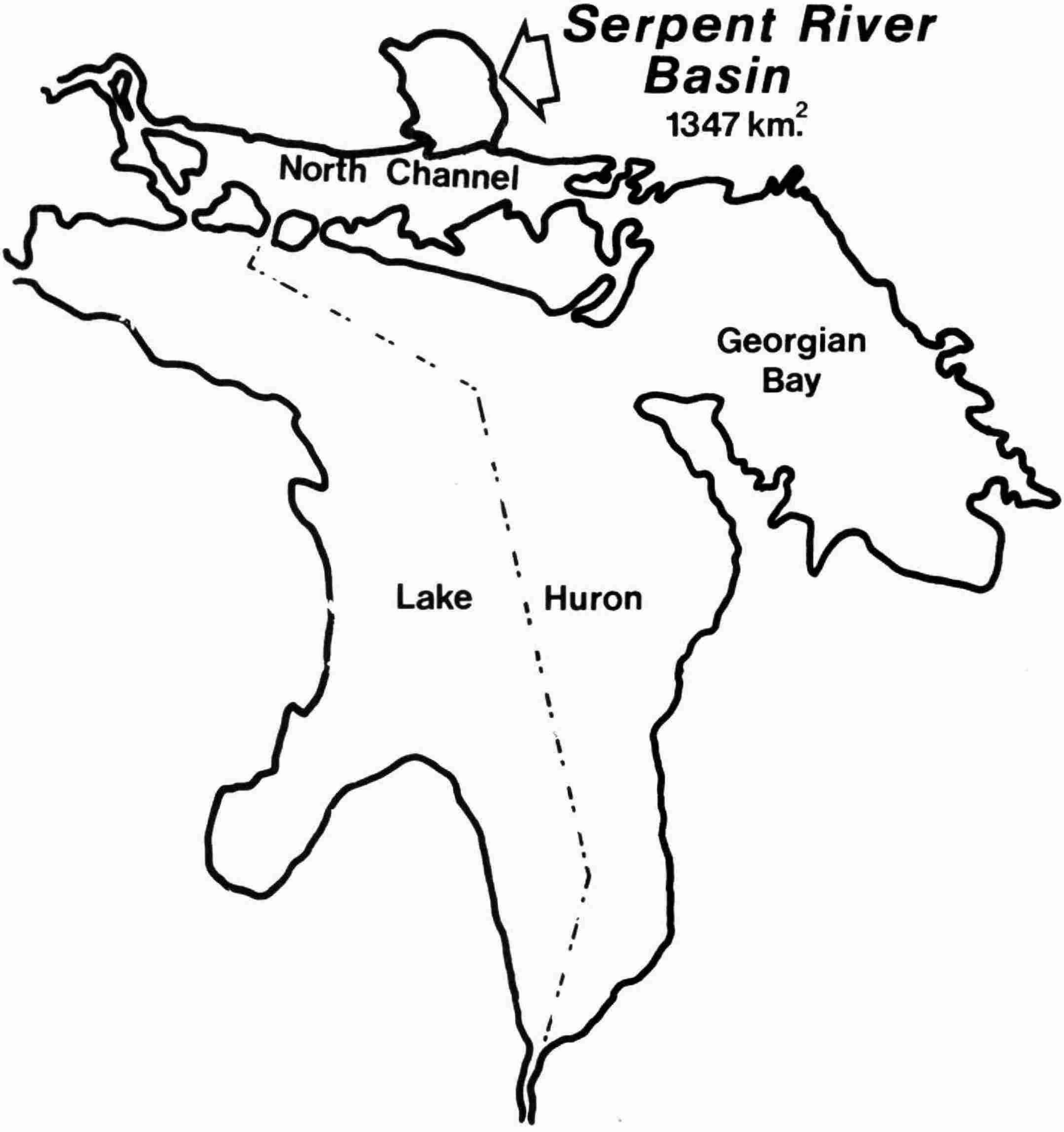
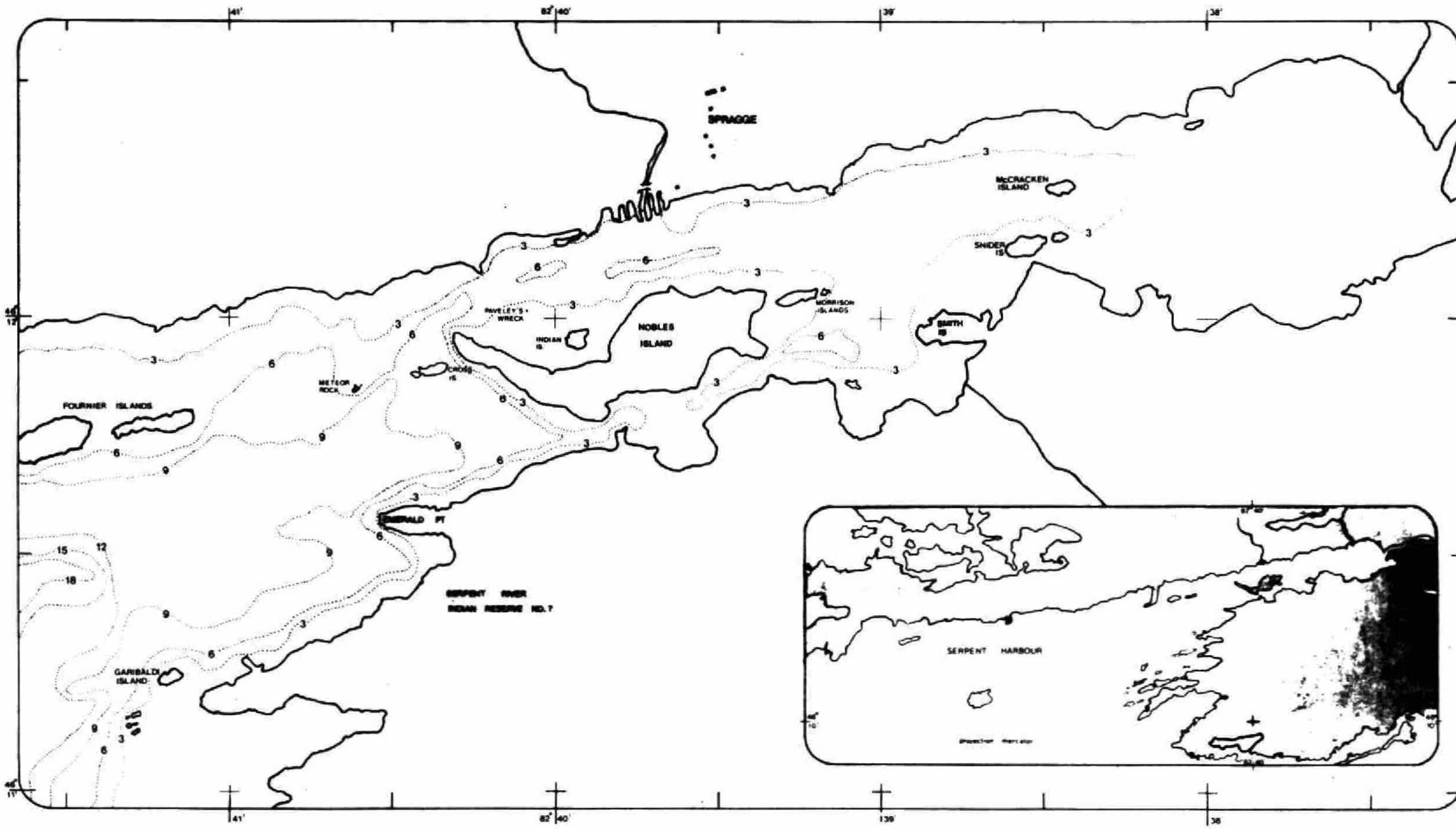

Serpent River
Basin
1347 km.^{2}
North Channel
Georgian
Bay
Lake
Huron

FIGURE 1



SERPENT HARBOUR

BATHYMETRY
Contour intervals - 3 metres
Depth as measured from chart datum

FIGURE 2

Based on Canadian Hydrographic Chart no. 2268

NORTH

PROJECTION POLYCONIC

pitation records (figure 3). A time lag between September rainfall at Elliott Lake and downstream discharges at Hwy.#17 in October is evident.

Total basin yield per year varied significantly from 1966 to 1974 ranging from a maximum of 7.3×10^5 acre-feet in 1970 to a minimum of 4.6×10^5 acre-feet in 1974 (5). Total basin yield and associated variability of seasonal discharges from year to year play governing roles in materials loading to the North Channel.

WATER USE

Prior to 1955, the principal water use in Serpent River Basin was the support of fish and aquatic life. Since the beginning of mining operations in the late 1950's, this industry has become the principal user of surface water.

Recreation

No formal public swimming areas exist on the harbour since access to the harbour by land is restricted, with roads servicing only the north shore.

At present the harbour services the small scale needs of pleasure boaters from the Elliot Lake area. North Channel Yacht Club is located on the north shore of the harbour, figure 4 . No public wharves or marinas presently exist in the harbour.

Water Supply

Domestic √

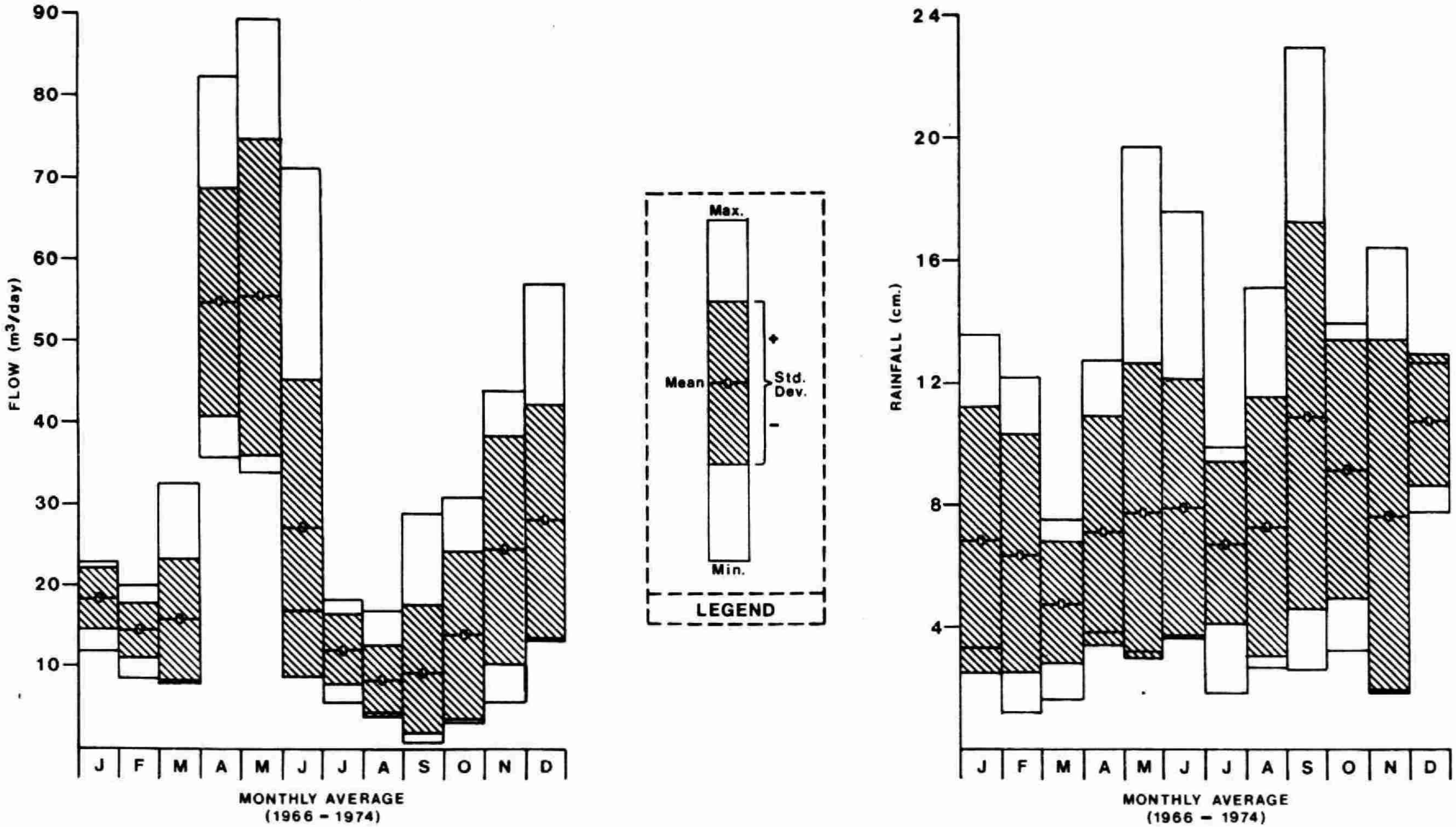
Table 1 summarizes water use (supply and disposal) in the area adjacent to Serpent Harbour. Three surface water intakes for domestic purposes exist in the area: North Channel Yacht Club, Town of Serpent River and south Rio Algom townsite.

Industrial √

The main user of surface water in the upstream Serpent River Basin is mining. The sole industrial water user in Serpent Harbour at present is the Reiss Lime plant. Although water intakes exist for the Pater and Pronto Mines, their use for water supply was terminated in 1970.

Domestic Sewage Disposal

Sewage treatment for homes adjacent to Serpent Harbour is on an individual or shared household basis. Table 1 summarizes the nature of sewage treatment for homes in the area. Multiple sewage treatment techniques such as lagoons, septic tanks, pit privies and cesspools are employed in the area.



SERPENT RIVER
STATISTICAL RECORD OF STREAM FLOW
(8.4 Km. from mouth)

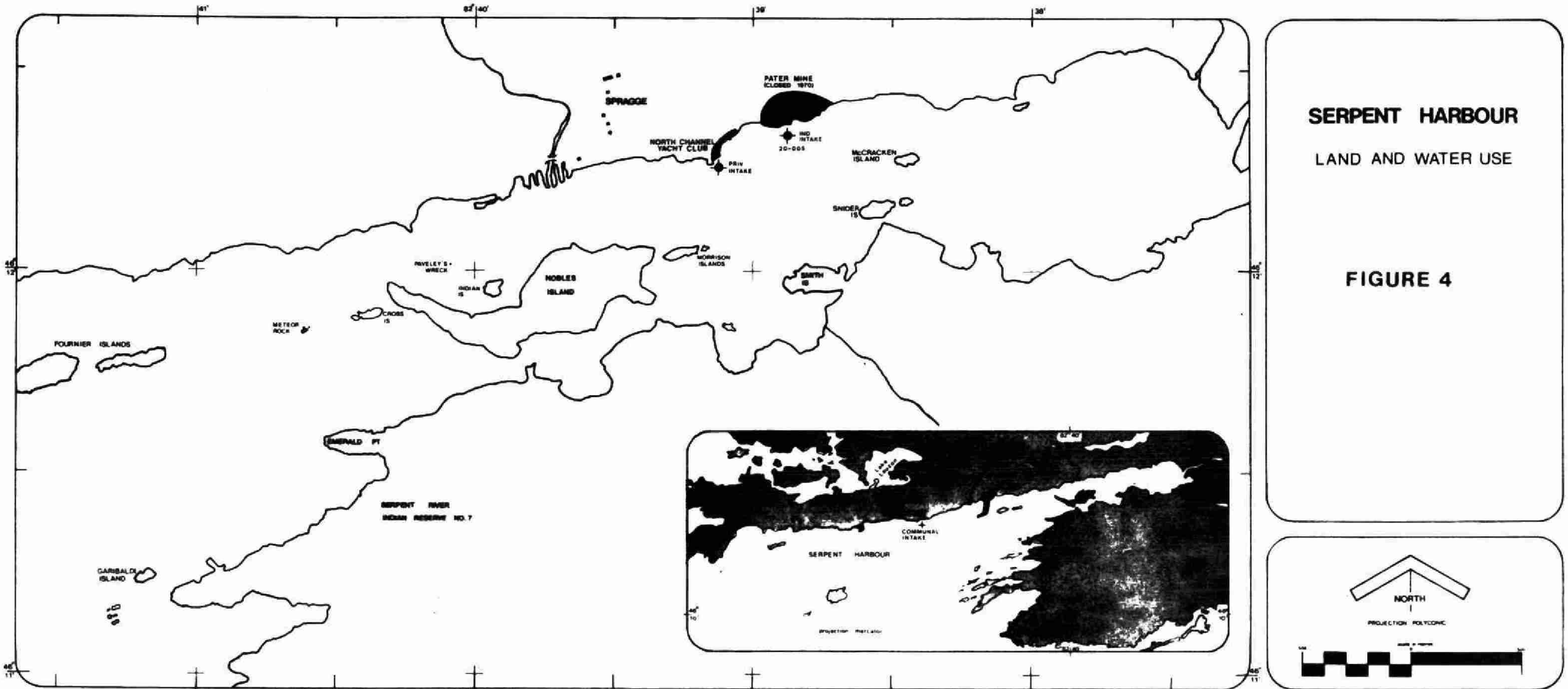
ELLIOT LAKE
COMPOUND HYETOGRAPH

FIGURE 3

TABLE 1 SERPENT HARBOUR WATER USE

LOCATION (town, village, townsite)	NUMBER USERS	WATER SUPPLY	WASTE DISPOSAL
Spragge (north side of Serpent Harbour)	109 homes (leased)	Individual household and combined household - private wells	Individual household and combined household systems - septic tanks, cesspools, pits.
	1 home and clubhouse.	1 private surface water supply in Serpent Harbour for North Channel Yacht Club.	
Town of Serpent River. (6.44 Km.upstream of river mouth)	100 homes (estimate)	Communal surface water supply from Serpent River.	Individual household systems - septic tanks, cesspools, pits.
Lake Lauzon Rio-Algom Townsite (8.05 Km. west Serpent River mouth)	18 homes (leased)	Communal surface water supply from Lake Lauzon	Individual household septic tank systems.
Rio Algom South Townsite (south of Hwy.17 8.05 Km. west of Serpent River mouth.)	19 homes	Communal surface water supply from North Channel.	Communal lagoon system with overflow to North Channel.
Algoma Mills (14.9 Km. west of Serpent River mouth).	80 homes	Individual household Shallow wells (10')	Individual household systems - septic tanks, cesspools and pits.
Reiss Lime Plant	1 plant	Intake from North Channel	Settling pond for plant and sanitary wastes.

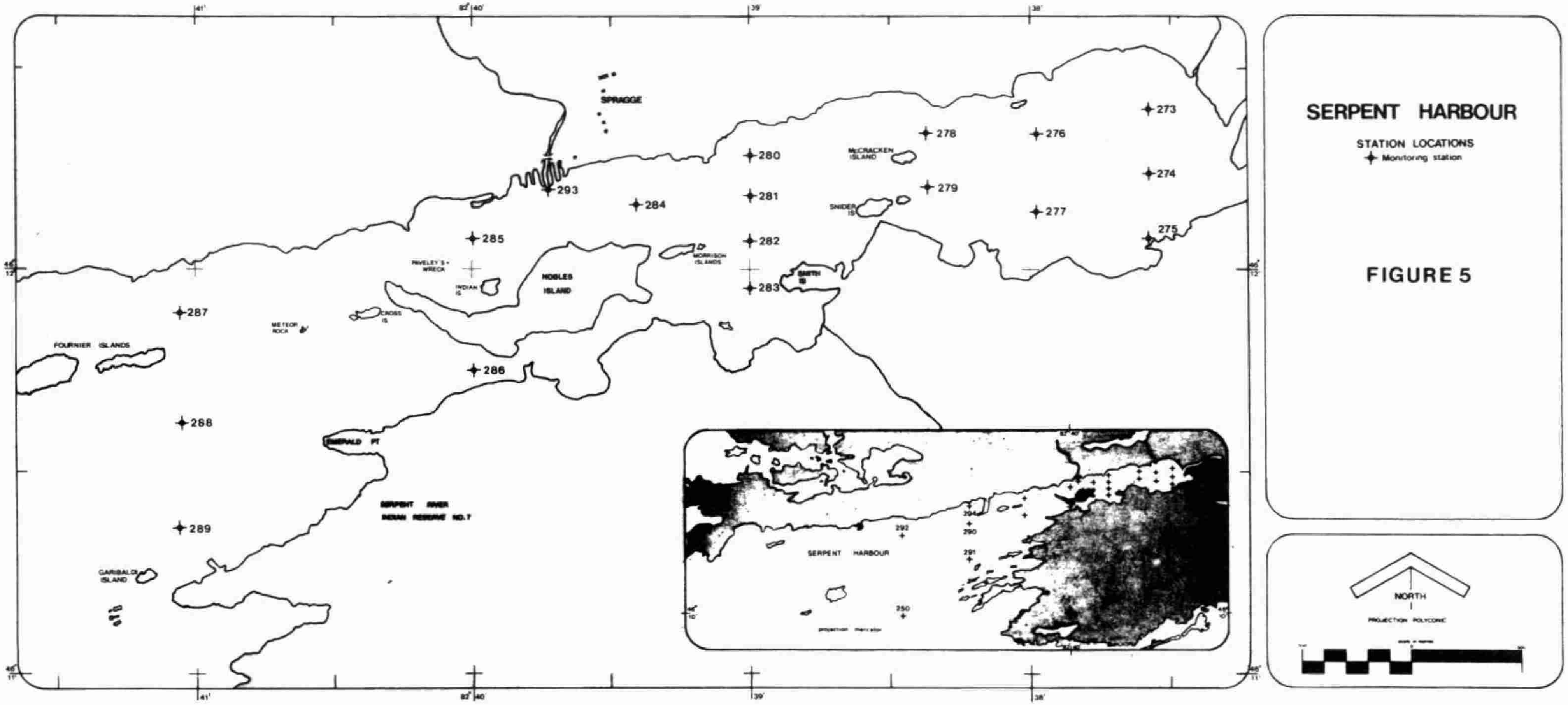
Source: Personal communication to I.Ross from N. Giguere, Algoma Health Unit, Blind River, Ontario, December 12, 1975.



SERPENT HARBOUR

LAND AND WATER USE

FIGURE 4



SERPENT HARBOUR
STATION LOCATIONS
Monitoring station
FIGURE 5
NORTH
PROJECTION POLYCONIC
41'
82° 40'
39'
38'
46° 12'
46° 11'
SPRAGGE
McCRACKEN ISLAND
SNIDER IS
MORRISON ISLANDS
SMITH IS
NOBLES ISLAND
PAVELEY'S WRECK
INDIAN IS
CROSS IS
METEOR ROCK
FOURNIER ISLANDS
EMERALD PT
SERPENT RIVER INDIAN RESERVE NO.7
GARIBALDI ISLAND
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SERPENT HARBOUR
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250

DISCUSSION

It was elected to approach the analysis of all available data on the basis of an input/output framework for which two distinct data divisions were created: (a) Materials input - Serpent River and Pronto Ditch; and (b) Serpent Harbour.

Analysis used in the materials input division was approached on a time series basis for two fixed point locations; Pronto ditch at Hwy.#17 and Serpent River at Hwy.#17. Analysis of water quality data for Serpent Harbour was approached on the basis of spatial trends and if applicable, temporal trends.

A variable length record of water quality data for up to 32 variables and 172 samples from 1966 to 1975 was used in loadings calculations at the Serpent River gauge located 8.4 km from the river mouth (Hwy.#17 at the Iron Bridge). Selected portions of the 5500 element data matrix are summarized in tables 2 to 5. Records for the federal flow gauge (02CD001), located at the same site of water quality sampling, were used in loading calculations. Flow data were extracted from the surface water data publications of Environment Canada (5).

The major materials considered in the loadings were; ^{226}Ra, gross α, gross β, total nitrogen, nitrate, ammonia, total phosphorus, sulphate, iron, total solids and suspended solids.

TABLE .2.

ESTIMATED TOTAL ANNUAL LOADINGS TO SERPENT HARBOUR FROM SERPENT RIVER

Year	Hardness $x10^3$ tonnes/yr.	Alkalinity $x10^3$ tonnes/yr.	Sulphate $x10^3$ tonnes/yr.	Total Nitrogen ($TKN + NO_2-N + NO_3-N$) $x10^3$ tonnes/yr.	Nitrate NO_3-N $x10^3$ tonnes/yr.	Ammonia NH_3-N tonnes/yr.	Total Solids $x10^3$ tonnes/yr.	Suspended Solids $x10^3$ tonnes/yr.	Total Iron tonnes/yr.	Total Phosphorus tonnes/yr.
1967	67.98	3.97	48.3	1.47	.82	418.	111.54	3.90	183	132
1968	48.14	3.06	39.3	1.41	.83	247	75.97	2.03	161	46
1969	42.04	3.79	50.5*	1.56	.82	318.	95.47	10.72	195	23
1970	52.56	5.76	48.6*	1.55	1.12	347	92.55	4.82	158	11
1971	30.36	3.80	28.9*	1.08	.64	258	54.42	3.74	113	11
1972	38.9	2.28	29.6*	1.27	.71	246	77.31	6.42	259	12
1973	IS	3.17	35.0*	1.14	.70	210	53.56	IS	185*	38
1974	IS	4.68	22.4*	1.03	.70	162	IS.	IS	103*	20

Note: - All data compiled for stream guage located 8.4 km. from Serpent River Mouth at Highway #17, stream guage station codes
- D.O.E. flows #02CD001
- OMOE water quality #14-0019-001-02

- tonne = metric ton = 10^3 kg

Formula Used:

$$Le = (\Sigma^{12} (\bar{Q} \times \bar{C}) \times K) \times D$$

where: Le = Annual Loading estimate (metric tonnes/yr.).
$\bar{Q}$ = Mean flow for month (cfs).
$\bar{C}$ = Mean variable concentration for month (mg/l).

K = Units conversion factor = 2.446.
D = Time and tonnes conversion factor = 3.0×10^{-2}.
n = Month.

* - Possible erroneous value due to small sample size.
IS- Insufficient sample size.

TABLE: 3 Estimated Total Annual Radiochemical Loadings to Serpent Harbour from Serpent River

Year	Total Radium 226 (diss. + undiss.) Curies ^{226}Ra/yr.	Total Gross Alpha (diss. + undiss.) Curies α/yr.	Total Gross Beta (diss. + undiss.) Curies β/yr.
1967	6.5	19.8	25.9
1968	5.7	20.3	23.0
1969	5.6	23.0	25.7
1970	6.0	24.3	29.0
1971	3.9	17.6	18.7
1972	4.3	10.5	13.8
1973	4.0	8.5	14.8
1974	3.5	9.0	9.0

Note: Data reported for station gauge located 8.4 km upstream of Serpent River Mouth at Hwy. 17, DOE Flow Gauge #02CD001; OMOE water quality station #14-0019-001-02.

Formula used:

$$Le = \left(\frac{\left(\sum_{1}^{n} Q \times C \times K\right) \times 12}{n} \right) \times D$$

where:

Le = Annual loading estimate (Curies/yr)
Q = Mean day flow at time of grab sample
C = Radioactivity level of grab sample (pCi/l)
K = Unit conversion factor (.002446507)
D = Time and Curies conversion factor (3.0×10^{-2})

TABLE 4

Annual Summaries for total ^{226}Ra pCi/l
Pronto Ditch at Hwy #17

Year	Min.	Max.	Arith. Mean	n	Std. Devn. (1σ)	Variance (σ2)	Σx
1966	11	20	15.6	10	3.2	10.04	156.0
1967	2.3	22	12.3	20	4.7	22.40	245.3
1968	2.0	22	13.9	14	5.8	33.16	194.5
1969	3.0	25	10.9	10	6.97	48.54	109.0
1970	-	-	-	No Data	-	-	-
1971	18	65	30.4	5	19.81	392.30	152
1972	3	30	10.6	10	9.78	95.60	106.
1973	1	8	4.3	13	2.32	5.40	56
1974	1	10	3.9	13	2.75	7.58	51

Annual Summaries for total gross alpha pCi/l
(dissolved and undissolved)
Pronto Ditch at Hwy 17

Year	Min.	Max.	Arith. Mean	n	Std. Devn. (1σ)	Variance (σ^2)	Σx
1966	32	99	52.9	10	19.70	388.09	529
1967	15	98	38.6	20	19.51	380.60	771.9
1968	34	122	73.4	14	31.60	998.86	1027.0
1969	6	96	61.4	10	27.91	779.16	614.0
1970	-	-	-	No Data	-	-	-
1971	15	420	140.0	5	160.04	25613.0	700
1972	7	85	26.5	10	23.30	542.94	265
1973	7	30	17.3	13	7.24	52.40	225
1974	2	58	15.5	13	14.32	204.94	202

Annual Summaries for total gross beta pCi/l
(dissolved & undissolved)
Pronto Ditch at Hwy #17

Year	Min.	Max.	Arith. Mean	n	Std. Devn. (1σ)	Variance (σ^2)	Σx
1966	30	74	44.58	10	13.22	174.71	445.8
1967	22	134	44.58	20	23.44	549.67	891.5
1968	32	104	70.79	14	22.75	517.72	991.0
1969	16	99	66.60	10	25.50	650.27	666.0
1970	-	-	-	No Data	-	-	-
1971	70	455	163.00	4	163.77	22821.50	815
1972	12	145	46.10	10	40.23	1618.77	461
1973	5	55	24.92	13	14.85	220.41	324
1974	7	61	19.38	13	14.68	215.42	252

Annual Summaries for Uranium 238 μg U^{238}/l
Pronto Ditch at Hwy #17

Year	Min.	Max.	Arith. Mean	n	Std. Devn. (1σ)	Variance (σ^2)	Σx
1966	16	142	33	10	38.56	1486.89	330
1967	10	120	20.7	20	25.07	628.66	413
1968	10	140	49.1	14	40.66	1653.36	688
1969	10	66	23.8	9	22.66	513.69	214
1970	-	-	-	No Data	-	-	-
1971	10	510	116	5	220.49	48617.5	580
1972	5	43	19	10	12.21	149.11	190
1973	10	51	20.9	13	14.11	199.14	271
1974	10	176	27.6	12	47.07	2215.72	331

Field Methods

From May 26 to May 30, 1975 a three day survey encompassing a grid of 23 water quality stations on Serpent Harbour, was completed (figure 5). During this study water samples were taken for nutrient, chemical, bacteriological and radio-chemical analysis. Grab and core samples were also taken for sediment analysis. Field methods, analytical methods and data coding were followed according to OMOE procedures (6,7 and 8). In addition, a survey during September 23, 1975 was undertaken to confirm the radioactivity levels within the harbour.

Bridge sampling was used at the two river sampling sites. All samples were submitted to the Ministry of the Environment Laboratory at Toronto for analysis with the exception of radiological samples which were analysed by the Radiation Protection Laboratory of the Ontario Ministry of Health.

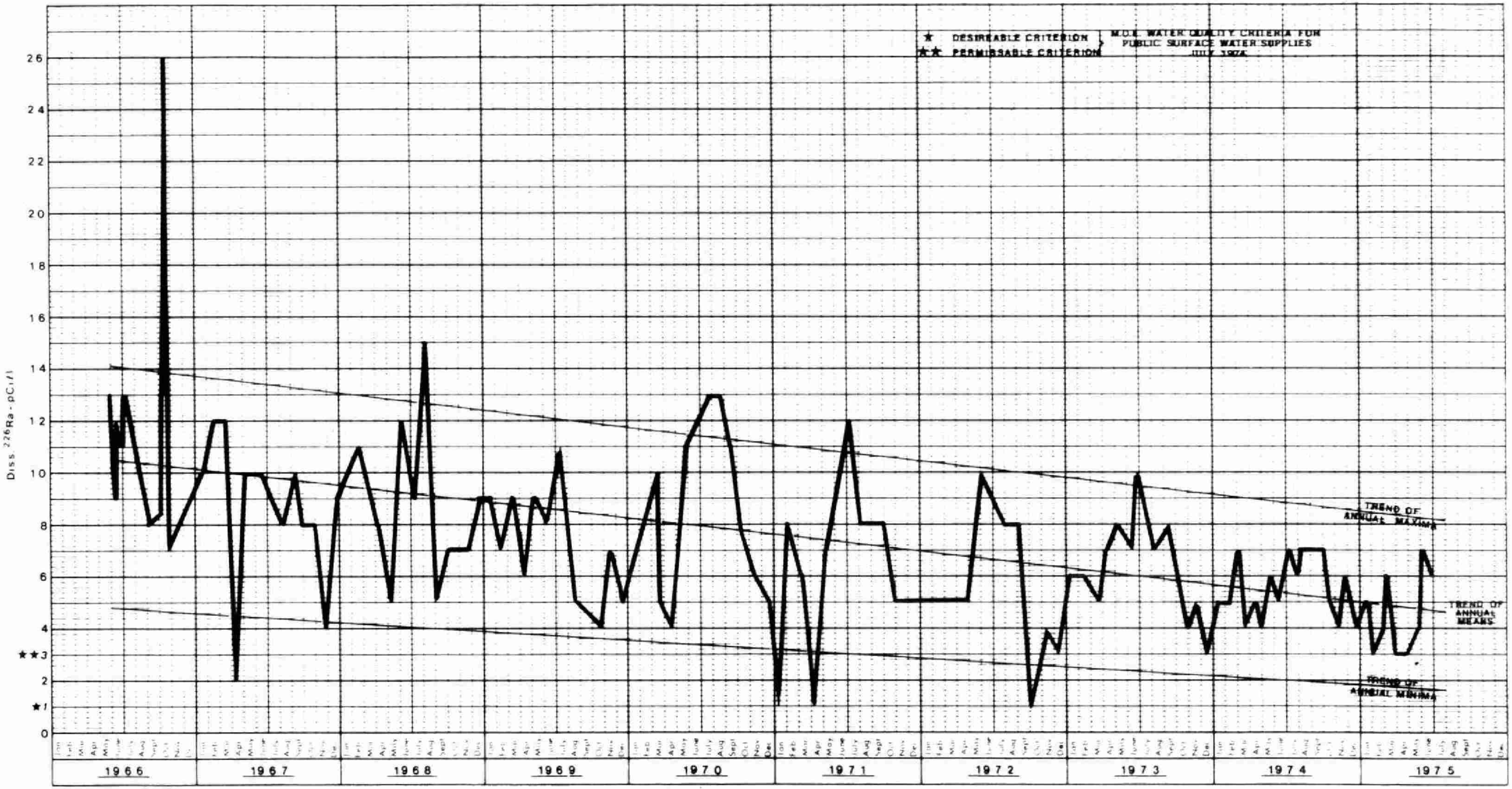
Radium 226

Serpent Harbour is the receiving basin for significant quantities of ^{226}Ra from two sources; 1) Serpent River and 2) Pronto Ditch. Serpent River accounts for about 98% of the total annual ^{226}Ra load to the harbour from the two sources.

Figure 6 and 7 demonstrate that significant decreases in ^{226}Ra levels and loadings from Serpent River have occurred over the period 1966 to 1974. However, levels have consistently averaged above 3pCi ^{226}Ra/l, the OMOE permissible criterion for public surface water supply (1). Waste management strategies employed at both active and inactive mine, mill and tailings areas are partially responsible for these trends. Present waste management strategies at these sites include:

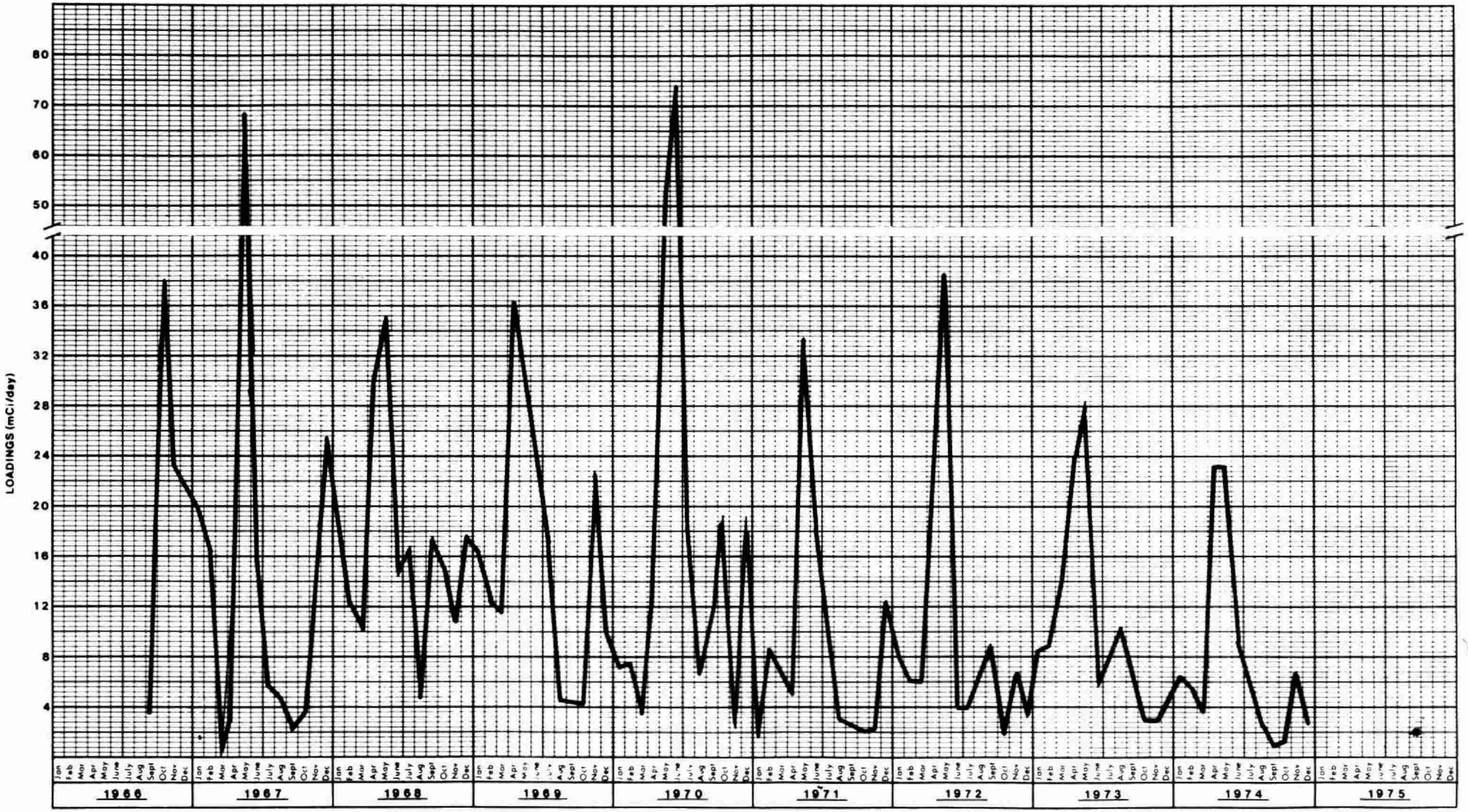
1) Barium chloride treatment
2) Elimination of direct discharges to receiving waters
3) Reuse of process waters
4) Application of lime to mill effluents for pH regulation
5) General housekeeping
6) Maintenance and improvement of tailing pond dyke structures

Application of statistical trend analysis suggested that further decreases in radium levels and loadings should occur. However, this analysis can be misleading due to a lack of consideration of other important variables. Further statistical analysis was undertaken to test a hypothesis for diminished ^{226}Ra levels and loadings to Serpent Harbour.



ANNUAL LEVELS OF ^{226}Ra FOR SERPENT RIVER – (8.4 Km. from mouth)

FIGURE 6



ANNUAL LOADINGS OF ^{226}Ra – SERPENT RIVER (8.4 Km. from mouth)

FIGURE 7

This hypothesis suggests that diminished tailings pond overflow and natural decreases in streamflow could be partially responsible for decreasing trends in radium levels and loadings. This hypothesis assumes that tailings ponds act as a pool of ^{226}Ra and that natural hydrologic events would govern losses to the Serpent River system. As such, the amount of snowmelt and precipitation would govern the magnitude of tailings pond seepage and overflow.

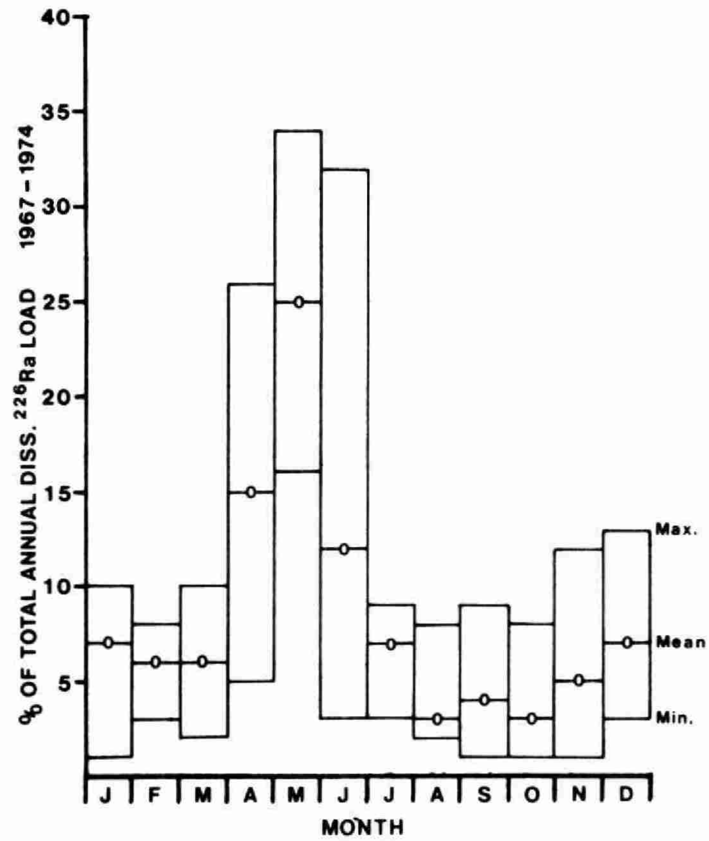
Figure 8 summarizes the range and mean of monthly percentages of annual radium loads over the period 1967 to 1974. The largest proportion of the annual ^{226}Ra load ($\sim$50%) in Serpent River occurs during a given year in the months of April, May and June; periods of snowmelt and highest river discharge. The time correlation between monthly percentage of annual ^{226}Ra load (figure 8) and monthly discharge (Figure 3) suggest that tailings pond flushing is expected to occur. The quantity of radium flushed from tailings ponds at operating and non-operating sites would be proportional to the magnitude of flow and storm events as demonstrated by the wide range of monthly percentage of annual radium loads during April, May and June.

Linear regression analysis was used to further verify the correlation between flow and the annual mean ^{226}Ra level. The correlation between total annual basin discharge in acre feet (x) and annual mean ^{226}Ra level (y) from 1966 to 1974 was statistically significant with r = .75. Serpent River streamflows at Hwy.#17 on an annual basis have diminished since 1967. The correlation suggests that natural decreases in streamflow are partially responsible for diminished ^{226}Ra levels and loadings to Serpent Harbour.

Regression analysis of total annual basin discharges in acre-feet (X) and annual ^{226}Ra variance (Y) was statistically significant (r = .92) and suggested that a large proportion of the annual variance in ^{226}Ra level is attributed to annual flows.

Figure 9 details the horizontal distribution of ^{226}Ra in harbour waters on May 30 and September 23, 1975. On May 30, 1975 an area within the harbour extending from the river mouth $\sim$5 km. had ^{226}Ra levels $\geq$3pCi/l (1). On September 23, 1975 ^{226}Ra levels were $\geq$3pCi/l (1) for an area extending $\sim$2.7 km from the river mouth.

Radium^{226} is quickly dissipated in Serpent Harbour as noted by lakeward gradients shown in figure 9. The nature of lakeward ^{226}Ra gradients is governed by the magnitude of tributary loads and harbour mixing, especially the effect of seiches. Radium 226 in natural waters is a very conservative variable. Levels measured at the Hwy.#17 monitoring station



MONTHLY PROPORTIONS OF TOTAL ANNUAL LOADINGS OF ^{226}Ra

SERPENT RIVER
8.4 Km. from mouth

FIGURE 8

TABLE 5

STATISTICAL SUMMARY OF SERPENT RIVER RADIOLOGICAL DATA FOR MINISTRY OF THE ENVIRONMENT MONITORING STATION #14-0019-001-02 8.4 Km. FROM HARBOUR

ANNUAL SUMMARIES FOR RADIUM 226 LEVELS PICOCURIES PER LITER

Year	MINIMUM	MAXIMUM	MEAN	# SAMPLES	STD. DEVIATION	VARIANCE
1966	7	26	11.7	12	4.95	24.53
1967	2	12	8.8	15	2.68	7.17
1968	5	15	8.8	14	2.69	7.26
1969	4	11	7.3	11	2.15	4.62
1970	4	13	8.7	12	3.31	10.96
1971	1	12	6.5	12	3.18	10.09
1972	2	10	5.7	12	2.61	6.79
1973	3	10	6.1	14	1.88	3.52
1974	4	7	5.5	17	1.18	1.39
1975	3	28	5.1	18	5.73	32.82
1976	4	6	5.5	3	1.15	1.33

8.4 km. up stream of the river mouth are therefore representative of levels occuring within the inner portions of Serpent Harbour.

Gross α Activity

As with radium loadings, the largest proportion of gross α (dissolved + undissolved) loadings to Serpent Harbour occur via the Serpent River. Loadings and levels for gross α are summarized in tables 3 and 4, which indicate overall diminishing trends.

The horizontal distribution of gross α levels in the surficial waters (.5m) of Serpent Harbour is shown in Figure 10 for two occasions in 1975. Lakeward trends of gross α on May 30, 1975 indicate that dilution did not occur within $\sim$4km from the river mouth. The horizontal trend for gross α on September 23, 1975 (Figure 10) indicated a larger source strength and more rapid dilution. The difference between the two concentration gradients is attributed to seasonal differences in Serpent River loadings.

Gross β Activity

Total gross β (dissolved + undissolved) loadings to Serpent Harbour have decreased since 1966 and demonstrate trends similar to those of ^{226}Ra (table 3). Over the period of record, gross β levels in individual samples in Serpent River (8.4 km from river mouth) have never exceeded the OMOE permissible criterion for surface water supply (1) and only one sample in 1968 exceeded the desirable criterion of <100 pCi/l.

The horizontal trends for gross β as a function of distance lakeward through Serpent Harbour are shown in Figure 11 for two occasions in 1975. Dilution patterns shown resemble closely those discussed for gross α. A log order of magnitude difference in gross beta levels is noted between the two surveys. Data for specific beta emitting radionuclides in Serpent Harbour is presently lacking and it is expected that other uranium daughter products may be present.

Uranium 238

Throughout the historical summary of U^{238} levels at Serpent River gauge (Hwy.#17), most levels have been reported at or less than the detection limit of 10 µg/l, therefore loadings have not been calculated. Uranium 238 levels in Serpent Harbour during the May survey were all reported <10µg/l.

HORIZONTAL DISTRIBUTION OF RADIUM 226 IN SERPENT HARBOUR

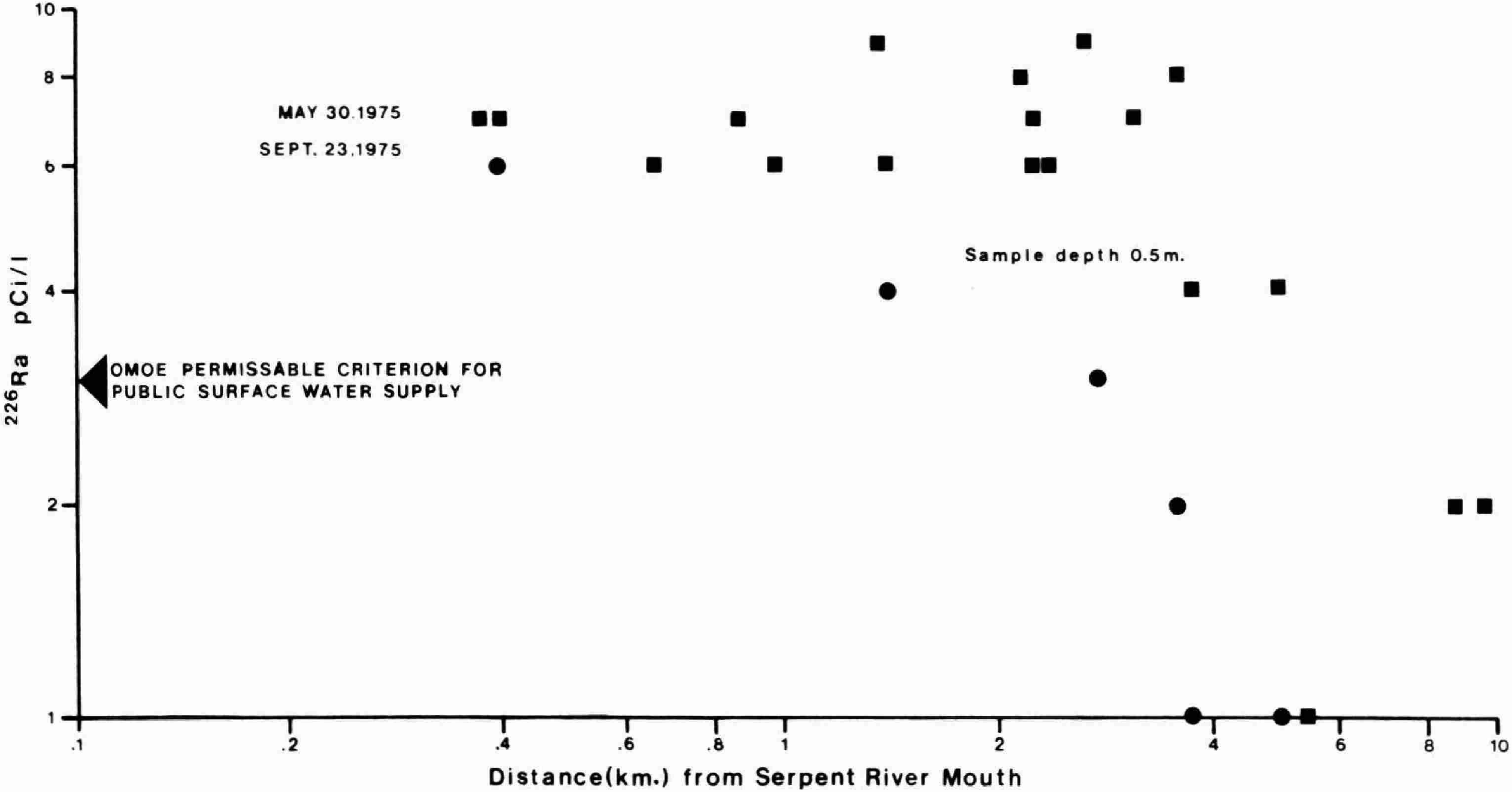


FIGURE 9

HORIZONTAL DISTRIBUTION OF GROSS α IN SERPENT HARBOUR

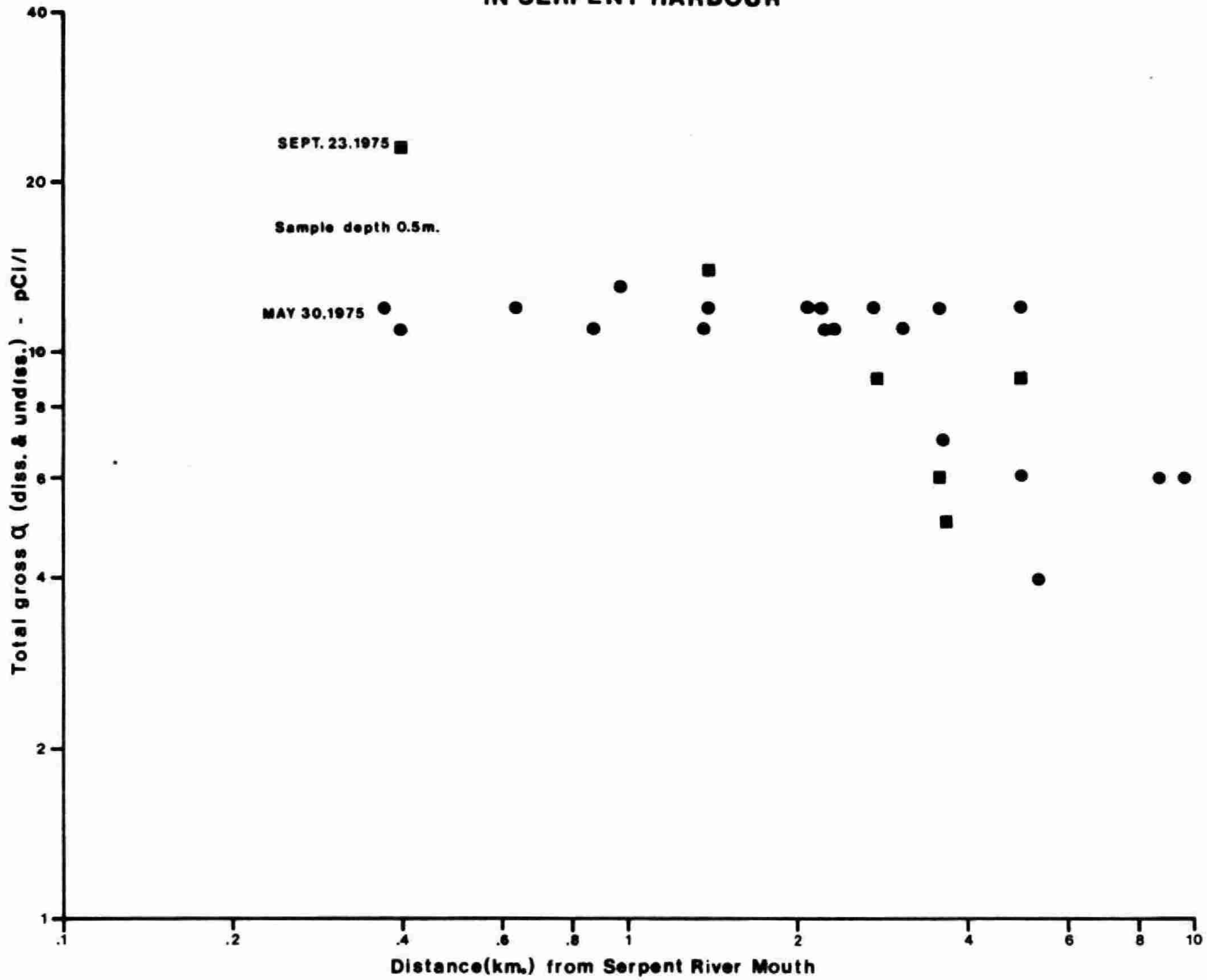


FIGURE 10

HORIZONTAL DISTRIBUTION OF GROSS β IN SERPENT HARBOUR

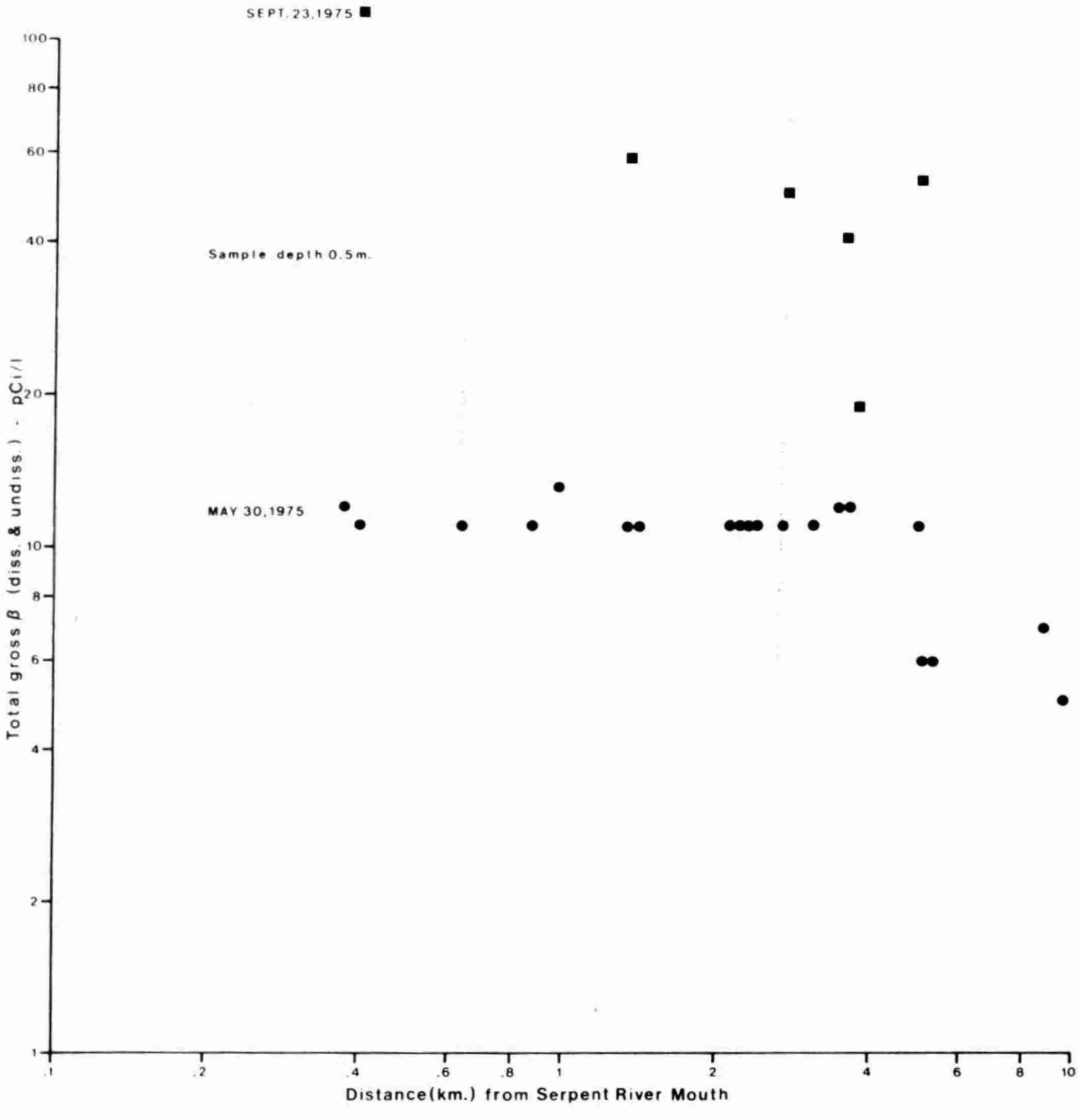


FIGURE 11

Table 4 details the historical record of U^{238} levels in Pronto ditch. Throughout the record high annual variances ranging over several log orders of magnitude are noted. Annual radiochemical loadings from this source account for only a small proportion (generally <3%) of the total loading to Serpent Harbour, primarily due to its small flow.

Dissolved Solids

Sulphate

Serpent Harbour receives significant loadings of sulphate as demonstrated by the range of annual loading estimates of 22.4×10^3 to 50.5×10^3 tonnes/yr. (table 2). The Serpent River Basin is characterized by geologic deposits of sulphide bearing ores. Mine activity extracts useful minerals (i.e. uranium) from these ores by dividing rock masses into finer sizes, extracting the wanted material and disposing remaining solids to retention ponds (tailings areas). Fine particles, due to increased surface area, are subject to an increased degree of microbial activity. Microbial activity in an acid environment increases the rate of oxidation of rock sulphides to water soluble sulphates. Overflow of tailings areas is likely to occur during peak rainfall and snowmelt periods, such that maximum annual loadings occur during the months of April and May.

Pronto ditch is significantly enriched with sulphate near its discharge to the North Channel, where 1974 levels ranged from 0 to >500mgSO_4/l. Although sulphate in Pronto ditch shows a far greater range in concentration than Serpent River, its sulphate loading is a small proportion of the total load entering the harbour from the two sources.

Figure 12 shows the horizontal distribution of sulphate in Serpent Harbour during the May 1975 cruise. Sulphate levels were uniformly at or near 40 mgSO_4/l within 4 km from the river mouth. Beyond 4 km, sulphate concentrations decreased dramatically and approached 20 mgSO_4/l at 9.5 km. It appears that the areal extent of sulphate off Serpent Harbour extends far beyond 10 km since sulphate concentrations in the North Channel are typically 13mg/l (9, 10).

Present sulphate levels in Serpent Harbour are within the OMOE desirable criterion of <50 mg/l for public surface water supply and do not appear to have any significant impact on local water use.

Chloride

Serpent River and Pronto Ditch are not significant sources of chloride; as such, a discussion of chloride loadings from this source is not forwarded. Figure 12 demonstrates the horizontal distribution of chloride in Serpent Harbour during the May 1975 cruise. Serpent Harbour has lower

HORIZONTAL DISTRIBUTION OF
SPECIFIC CONDUCTANCE, SULPHATE AND CHLORIDE
IN SERPENT HARBOUR
MAY 26 to 29, 1975

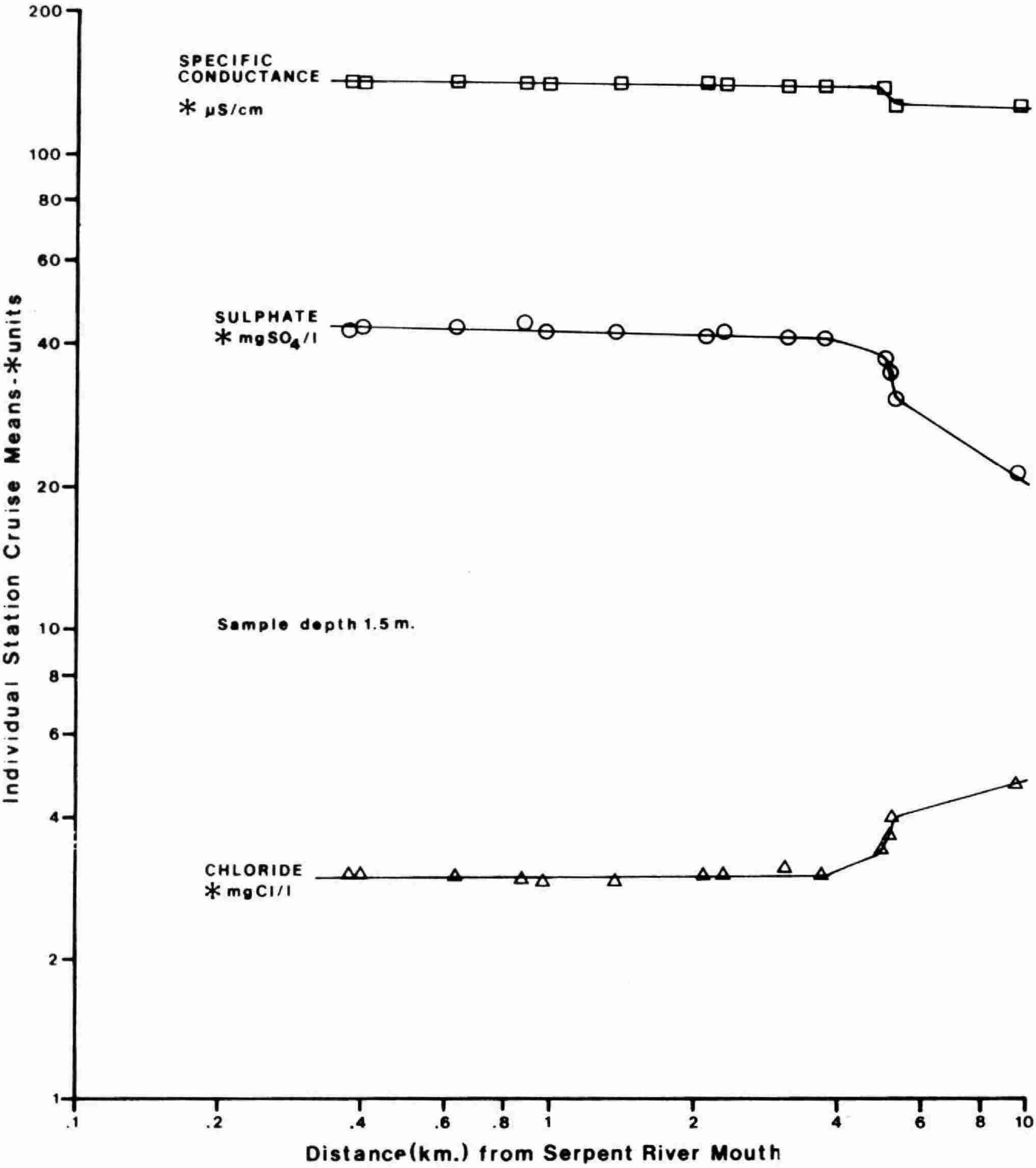


FIGURE 12

chloride concentrations than adjacent North Channel as a result of negligible tributary load. Chloride was uniformly distributed within the harbour at an average concentration of 3 mgCl/l which extended ∿ 4km from the river mouth. A trend toward a moderate increase in levels is indicated beyond 4 km which eventually approached background North Channel concentrations of 4.3 ± .7 mgCl/l (9,10).

Specific Conductance

The horizontal trend of specific conductance in Serpent Harbour during the May 1975 cruise is shown in Figure 12. No significant spatial differences were noted for levels within the Harbour since conductivity was uniformly at or near 140 μS/cm up to 5 km from the mouth. Beyond 5 km, levels diminished to 125 μS/cm at 10 km. The decreasing lakeward gradient in conductivity beyond 5 km is primarily attributed to diminished sulphate levels as a result of dilution and conversely a slight increase on chlorides as noted above.

Enrichment

Serpent River is a significant source of nitrogen loading to the harbour. Chlorophyll a and heterotrophic bacteria were elevated above background levels during the May 1975 cruise which suggests that Serpent Harbour is a potential enrichment problem area.

Nitrogen

A large proportion of the nitrogen input to the Serpent River system is a direct result of upstream uranium mining and milling activity in the Elliot Lake area. Estimated annual loading summaries shown in Table 2 for total nitrogen, nitrate and ammonia indicate that Serpent Harbour receives substantial quantities of nitrogen. Trend interpretation of the loading data from 1966 to 1974 indicates slight decreases in total annual nitrogen and nitrate loadings and small decreases in annual ammonia loadings with time.

Figure 13 demonstrates the horizontal distribution of nitrate, nitrite, ammonia and total Kjeldahl nitrogen (TKN) as a function of distance lakeward from Serpent River mouth during May 1975. All measured forms of nitrogen with the exception of nitrite showed diminishing lakeward gradients from the source of discharge. As with dissolved solids gradients previously described, inner harbour stations within 4 km of the source showed uniform cruise mean concentrations for nitrate, ammonia and TKN. Beyond 4 km the various forms of nitrogen with the exception of nitrite showed rapid dilutional gradients. The increasing gradient in nitrite concentration beyond 4 km is primarily attributed to the oxidation of ammonia to nitrite by nitrifying bacteria.

The introduction of nitrogen to the Serpent River system is primarily governed by the quantity of nitrogen used in the

HORIZONTAL DISTRIBUTION OF VARIOUS NITROGEN FORMS IN SERPENT HARBOUR MAY 26 to 29, 1975

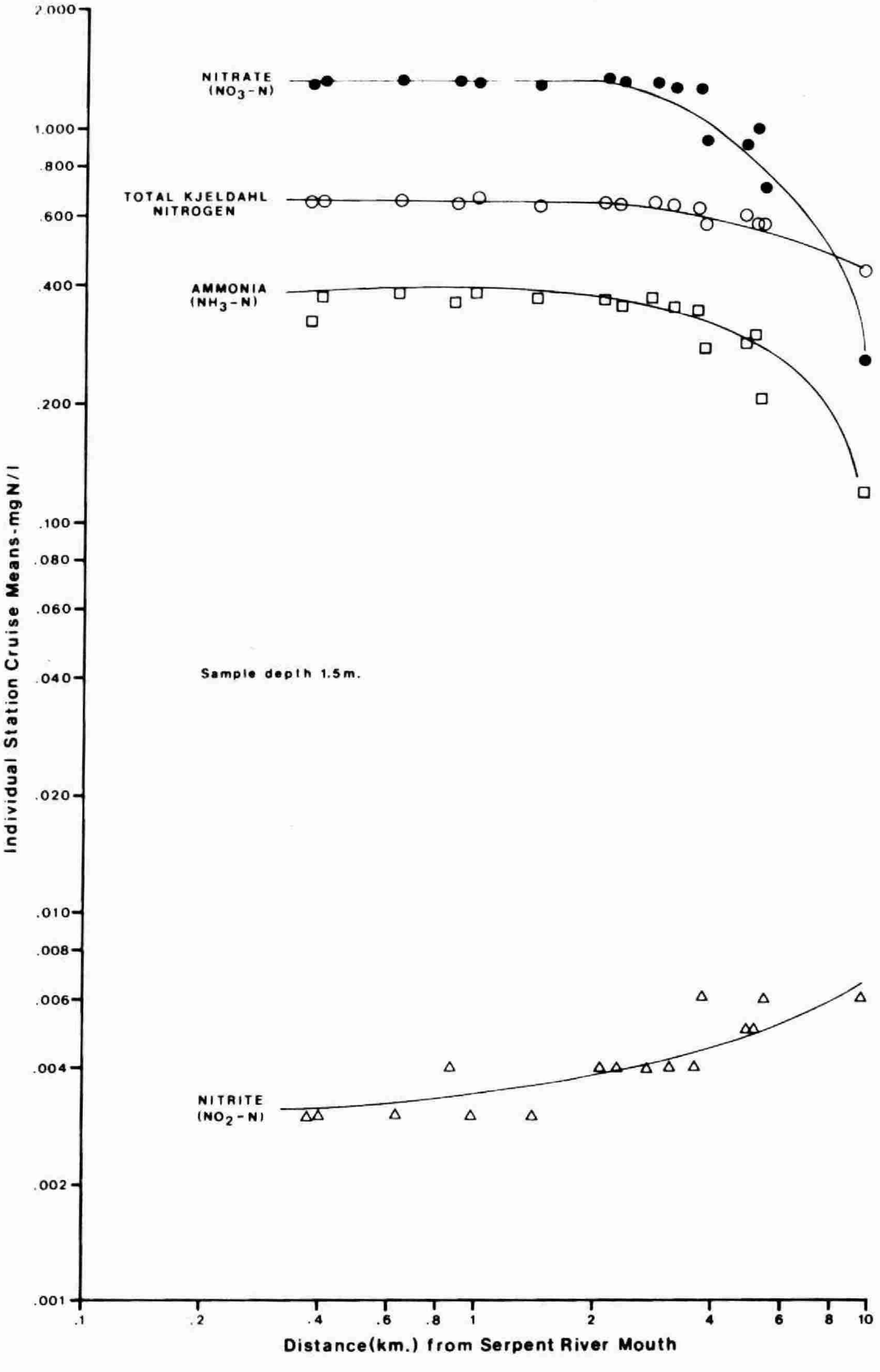


FIGURE 13

uranium extraction process. Process waste waters enriched with nitrogen are discharged to tailings ponds through which seepage to the Serpent River System occurs.

Phosphorus

Total phosphorus loading to Serpent Harbour is of a minor nature with the bulk of phosphorus being derived from natural land drainage as indicated by annual total phosphorus loadings shown in Table 2. The horizontal distribution of total and dissolved phosphorus in Serpent Harbour shown in Figure 14 suggests that phosphorus concentrations are lower in the harbour than in the adjacent North Channel (May 1975 Harbour mean total phosphorus .006 ± .002 mgP/l; and spring 1974 North Channel mean total phosphorus .012 ± .008 mgP/l (9,10).

Chlorophyll

Chlorophyll, a pigment in aquatic plants, is useful as an indicator of algal biomass. The horizontal distribution of chlorophyll α and β in Serpent Harbour during the May 1975 survey is shown in Figure 15. Both chlorophyll α and β concentrations increase at 5 km from the river mouth. The distribution of chlorophyll α and β within 5 km was highly variable ranging from 1.2 to 1.9 μg chlorophyll α/l and .5 to 1.4 μg chlorophyll β/l respectively.

There are several factors governing the variability of chlorophyll α and β distributions within the harbour, these include; 1) inhibition of growth due to the presence of high ammonia concentrations; 2) near neutral pH and a wide range in buffering capacity and 3) the increasing lakeward gradients for dissolved phosphorus (Figure 14).

There has been much discussion (11,12,13) regarding the use of chlorophyll α concentrations as indices of trophic status and it is generally conceeded that a level of 2 to 4 μg chlorophyll α/l is indicative of trends towards mesotrophic conditions. Without long term chlorophyll α data, it is difficult to project the present trophic status of Serpent Harbour. However, considering nitrogen loadings, the configuration of the harbour, chlorophyll α levels and the presence of moderately high heterotrophic bacterial populations (Figure 17), Serpent Harbour is identified as a potential enrichment problem area requiring further surveillance.

Alkalinity, Hardness and pH

Acid mine drainage has been an ongoing problem in the Serpent River drainage basin since the development of the uranium mining industry in the Elliot Lake area. An earlier OWRC report (3) recommended the need for pH regulation in mine effluents discharging to tailings areas. Presently, lime is being used for pH regulation at active and inactive

HORIZONTAL DISTRIBUTION OF PHOSPHORUS IN SERPENT HARBOUR

MAY 26 to 29, 1975

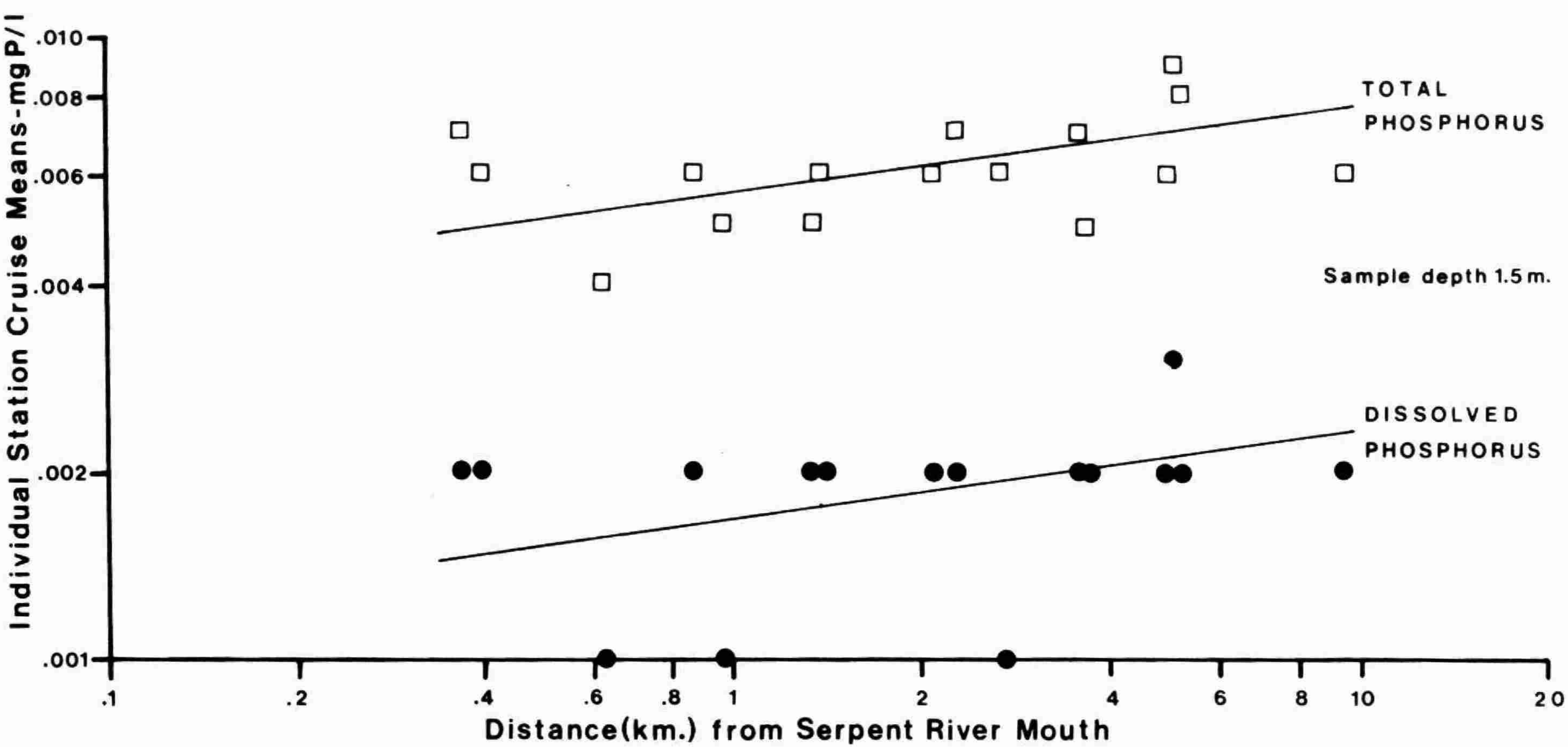


FIGURE 14

HORIZONTAL DISTRIBUTION OF CHLOROPHYLL a AND b
IN SERPENT HARBOUR
MAY 26 to 29, 1975

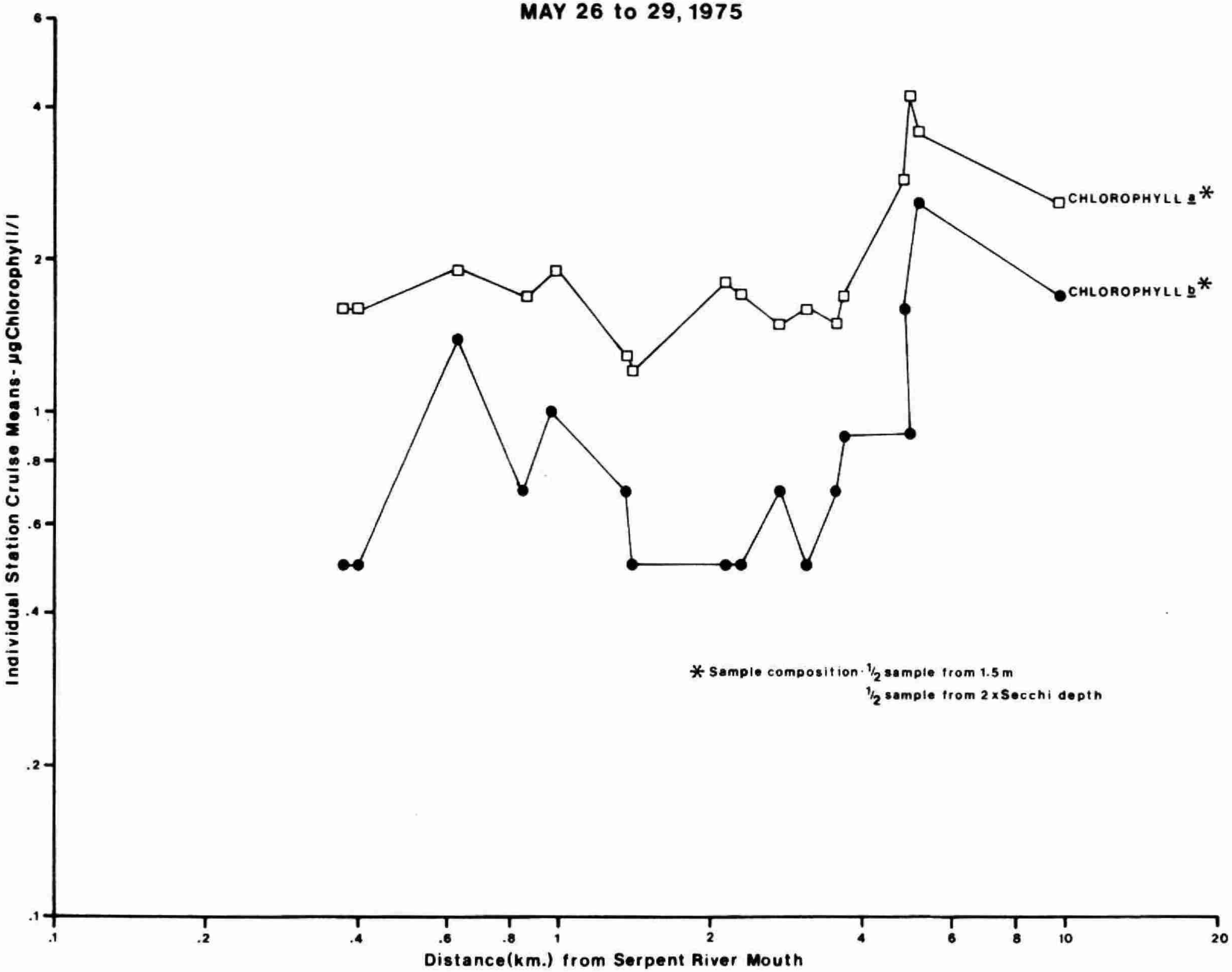


FIGURE 15

HORIZONTAL DISTRIBUTION OF HARDNESS AND ALKALINITY
IN SERPENT HARBOUR
MAY 26 to 29, 1975

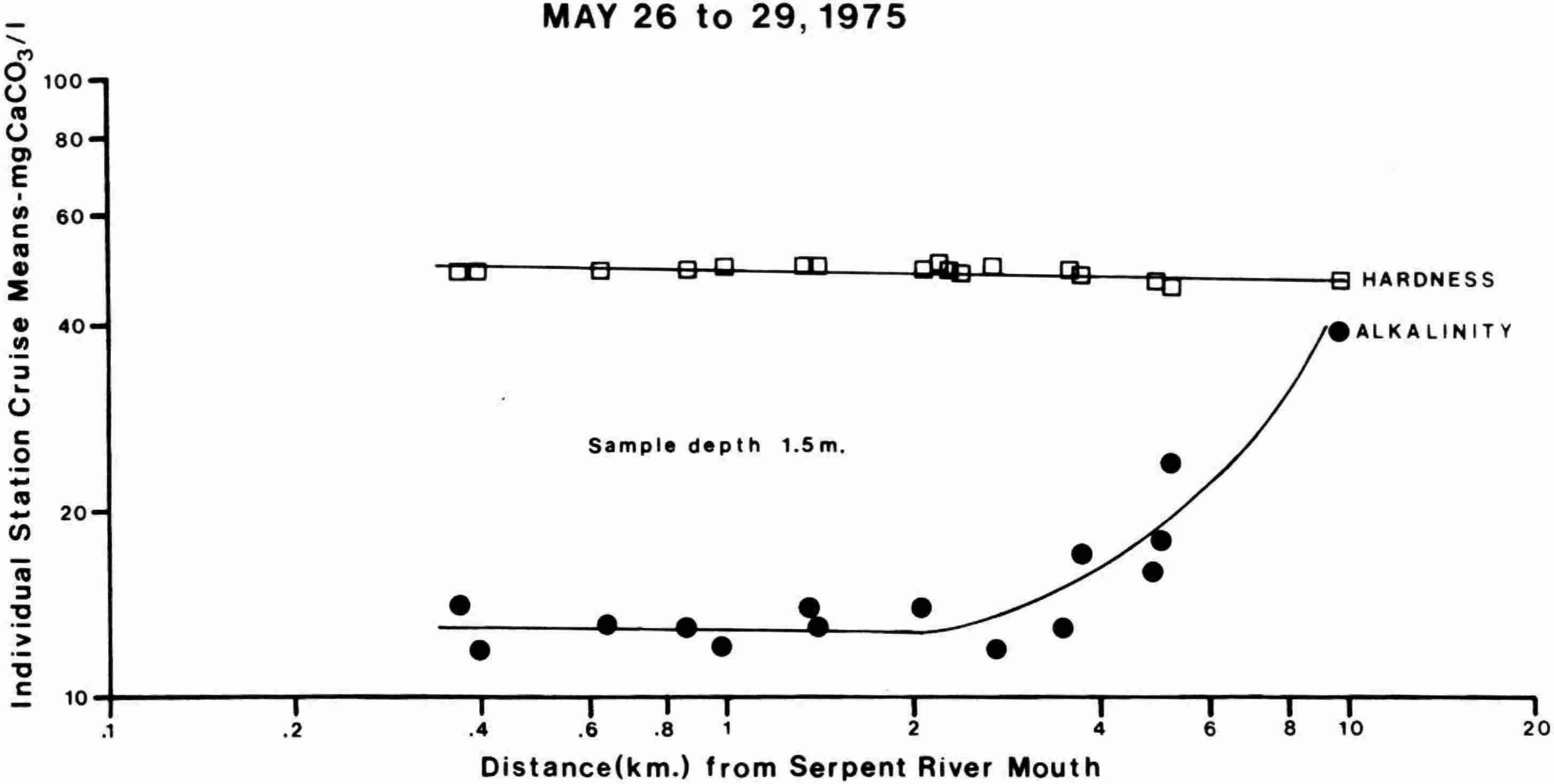


FIGURE 16

mill and tailings areas.

Table 2 summarizes estimated annual loadings of hardness and alkalinity to Serpent Harbour. As is evident from the data, Serpent River waters are low in carbonates, primarily due to the absence of carbonaceous rocks in the drainage basin. The significance of carbonates is the governing role they play in regulating the aquatic carbonate-bicarbonate buffering system.

Figure 16 shows the horizontal distribution of hardness and alkalinity in Serpent Harbour during May 1975. Hardness was uniformly distributed throughout the harbour with levels at or near 50 $mgCaCO_3/l$. A significant trend was noted in the distribution of alkalinity with suppressed levels at or near 13 $mgCaCO_3/l$ within 3 km from the river mouth. Beyond 3 km, alkalinity levels increased to 40 $mgCaCO_3/l$ as harbour waters mixed with offshore waters.

A suppression of pH was noted within the harbour with a cruise mean pH of 7.1 at station 273 near the mouth and a cruise mean pH of 7.5 at outermost station 250. Although present pH data were within acceptable limits for the protection of fish and other aquatic life, alkalinity levels were below the limits suggested to protect the carbonate system (< 20 $mgCaCO_3/l$; (1)). During the May survey, an area extending $\sim$ 5 km from Serpent River mouth had total field alkalinity levels $\leq$ 20 mg/l.

Dissolved Oxygen

Ample stocks of dissolved oxygen were present in the surficial (1.5 m) waters of the harbour during the May 1975 cruise where station mean dissolved oxygen levels and percent oxygen saturation values ranged from 8.9 to 11.0 mgO_2/l and 94 to 104% respectively.

Transparency

May 1975, cruise data did not indicate any problems associated with suspended solids, with station mean turbidity and Secchi depths ranging from 1 to 1.7 FTU (formazin turbidity units) and 1.6 to 2.0 m respectively. In addition, annual total and suspended solids loading estimates shown in Table 2 suggest some overall net decreases since 1967.

Water Microbiology

Figure 17 details the lakeward trends of individual station geometric means of heterotrophic bacteria, total coliforms, fecal coliforms and fecal streptococci during the May 1975 cruise. Geometric means of total coliforms, fecal coliforms and fecal streptococci were within OMOE recreational water use criteria (1) and specific Water Quality Agreement objectives (14). Moderately high heterotrophic bacteria populations characterized the bacterial flora of the harbour during the May 1975 cruise and are probably associated with

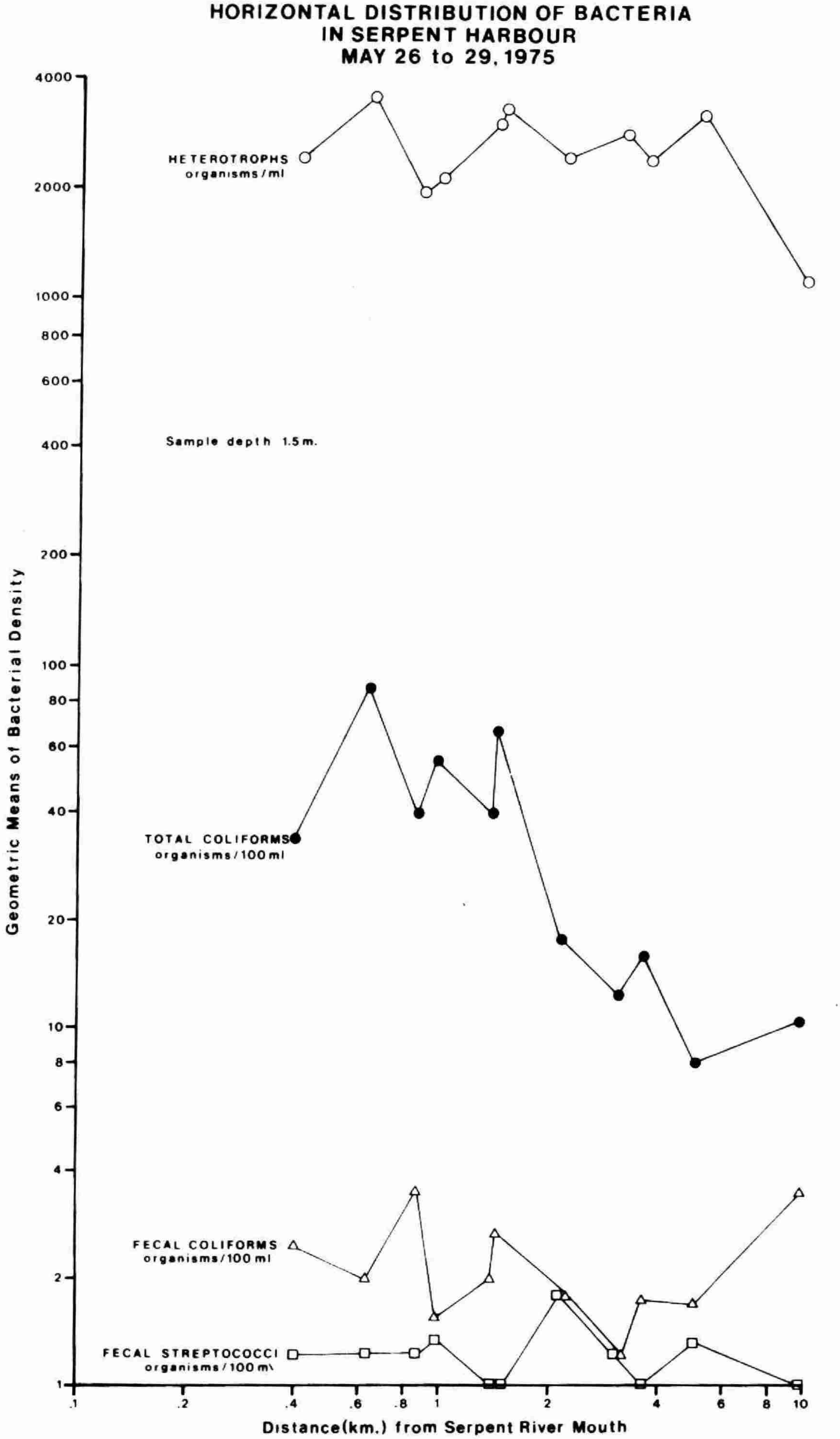

HORIZONTAL DISTRIBUTION OF BACTERIA
IN SERPENT HARBOUR
MAY 26 to 29, 1975
HETEROTROPHS
organisms/ml
Sample depth 1.5 m.
TOTAL COLIFORMS
organisms/100 ml
FECAL COLIFORMS
organisms/100 ml
FECAL STREPTOCOCCI
organisms/100 ml
Geometric Means of Bacterial Density
Distance(km.) from Serpent River Mouth
4000
2000
1000
800
600
400
200
100
80
60
40
20
10
8
6
4
2
1
.1
.2
.4
.6
.8
1
2
4
6
8
10

FIGURE 17

the presence of high nitrate, sulphate, total Kjeldahl nitrogen and ammonia nitrogen concentrations.

Heavy Metals in Water

Results of heavy metals analyses (Table 6) indicate that there were no significant differences in the horizontal distribution of total chromium, total cadmium, total lead, total zinc, total nickel and total cobalt. In most cases, all reported levels were at or near the detection limit of the analytical method (atomic absorption spectrophotometry (6)). Total iron concentrations throughout the harbour were of relatively uniform distribution. Table 2 gives estimates of annual total iron loadings to the harbour for which some year to year differences are noted. Present total iron levels within the harbour do not suggest any water use conflicts since data are an order of magnitude less than the OMOE permissible criterion of 0.3mg/l for public surface water supply (1).

Sediment

On May 30, 1975 extensive sediment sampling was undertaken encompassing a grid of 20 stations within Serpent Harbour (Figure 5). Both Phleger gravity coring (1.5" I.D.) and Ponar grab sampling was undertaken. Single gravity cores were obtained from stations 285, 281, 279, 277 and 274. The cores were segmented into four 5 cm sections up to 20 cm and submitted to the Radiation Protection Laboratory of the Ontario Ministry of Health for radiochemical analyses (Table 8). Core texture with depth was uniform at all five sites and consisted of fine dark gray silt.

Ponar grab samples were taken at 20 stations within the harbour. Grab samples were composited from a minimum of two similar samples per station using the top 5 cm of sediment from each cast. Sediment composition was relatively uniform at all stations consisting of fine dark grey silt. Sediment beyond 5 km from the river mouth had a thin (0-0.5 cm) overlay of golden brown silt at the sediment/water interface indicative of oxidized iron and implying bottom oxygen saturation conditions (15). All grab samples were submitted to the OMOE Main Laboratory in Rexdale, Ontario for heavy metal, nutrient, pesticide and PCB analysis. Analyses of grabs for ^{226}Ra, U^{238}, gross α and gross β were completed by the Radiation Protection Laboratory of the Ontario Ministry of Health, Toronto. Studies to assess the environmental and/or public health significance of sedimented contaminants were not undertaken at this time.

For the following section, data are summarized in Tables 7 to 12 and Figures 18 and 19. Concentrations of heavy metals and radioactivity levels along transects perpendicular to the length of the harbour had wide variations indicating that contaminant accumulation in sediment within the harbour was highly differentiated. To account for the variability of sedimentation within the harbour, two pathways were identified; 1) the pathway for maximum cross-sectional concentrations which predominated at stations

Table 6

Serpent Harbour

Heavy Metals in Surface Water

May 29, 1975

Station	Chromium µg Cr/l	Cadmium µg Cd/l	Lead µg Pb/l	Zinc µg Zn/l	Nickel µg Ni/l	Cobalt µg Co/l	Copper µg Cu/l	Total Iron mg Fe/l $\overline{X}$ (n)
275	<.04	<.01	<.02	.02	<.02	<.04	<.01	.13(8)
276			<.01	<.02				.15(8)
277				<.02				.15(8)
278				.03				.16(8)
279	<.01			.02				.15(8)
280	<.04			.02				.17(8)
281				.02				.17(8)
282				.03				.15(8)
283				.02				.17(8)
284				.02				.17(8)
293				.02				.20(7)
285				.02				.17(8)
286				.02	.04			.16(8)
287				.02	<.02			.16(8)
288				.01	.02			.16(8)
289				.01	.04			.18(8)
294				.02	<.02			N.D.
290				.02	<.02			.17(7)
291				.01	.03			N.D.
292				.01	.02			N.D.
250				<.01	.03			.16(7)
273	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	.16(8)
274	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	.14(8)

Note: - All samples taken at 1.5m from surface by immersion of plastic sample jars.
- Sample preservation and analysis in accordance with OMOE publication, "Outlines of Analytical Methods" February 1975 (6).

- N.D. - no data.

- all values for total metals (non speciated)

TABLE 7

SERPENT HARBOUR

RADIOACTIVITY AND NITROGEN IN SURFICIAL SEDIMENTS

MAY 30, 1975

PARAMETER	GEOMETRIC MEAN	SAMPLE SIZE	+S.D.	-S.D.	MIN.	MAX.
Gross α pCi/g (dry)	109	20	239	50	25	320
Gross β pCi/g (dry)	98	20	172	56	40	210
^{226}Ra pCi/g (dry)	28	20	64	12	7	91
^{238}U μg/g (dry)	37	20	66	21	14	86
Total Kjeldahl mg/gm Nitrogen	1.9	20	3.2	1.2	0.5	3.0
% loss on ignition	5.7	20	9.6	3.4	1.4	11

<u>Note</u>: - All data for recent surficial (0-5 cm) sediments in harbour encompassing an area of 4.14 km^2.
- All samples composited from similar duplicate Ponar grab samples.
- Harbour sediment of uniform composition-fine dark grey silt.
- All radioactivity analyses done by Radiation Protection Laboratory, Ontario Ministry of Health.

TABLE 8

SEDIMENT CORE RADIOACTIVITY

SERPENT HARBOUR

May 30, 1976

STATION	CORE DEPTH cm	GROSS α pCi/g (dry)	GROSS β pCi/g (dry)	^{226}Ra pCi/g (dry)	URANIUM μg/g (dry)
285	0- 4.9	40	45	10	29
	5- 9.9	15	25	1	15
	10-14.9	10	20	1	21
	15-19.9	5	20	1	13
281	0- 4.9	75	60	18	30
	5- 9.9	15	20	2	13
	10-14.9	15	20	2	10
	15-19.9	10	20	1	17
279	0- 4.9	30	35	10	23
	5- 9.9	20	25	2	19
	10-14.9	15	25	2	19
	15-19.9	15	25	2	14
277	0- 4.9	120	95	24	42
	5- 9.9	15	25	2	14
	10-19.9	10	25	2	14
	15-19.9	10	20	1	14
274	0- 4.9	70	65	20	31
	5- 9.9	10	25	3	13
	10-14.9	10	25	2	13
	15-19.9	20	30	3	18

* All samples collected with 1.5"I.D. Phleger Gravity Corer

** Analyses by Radiation Protection Laboratory, Ontario Ministry of Health, Toronto.

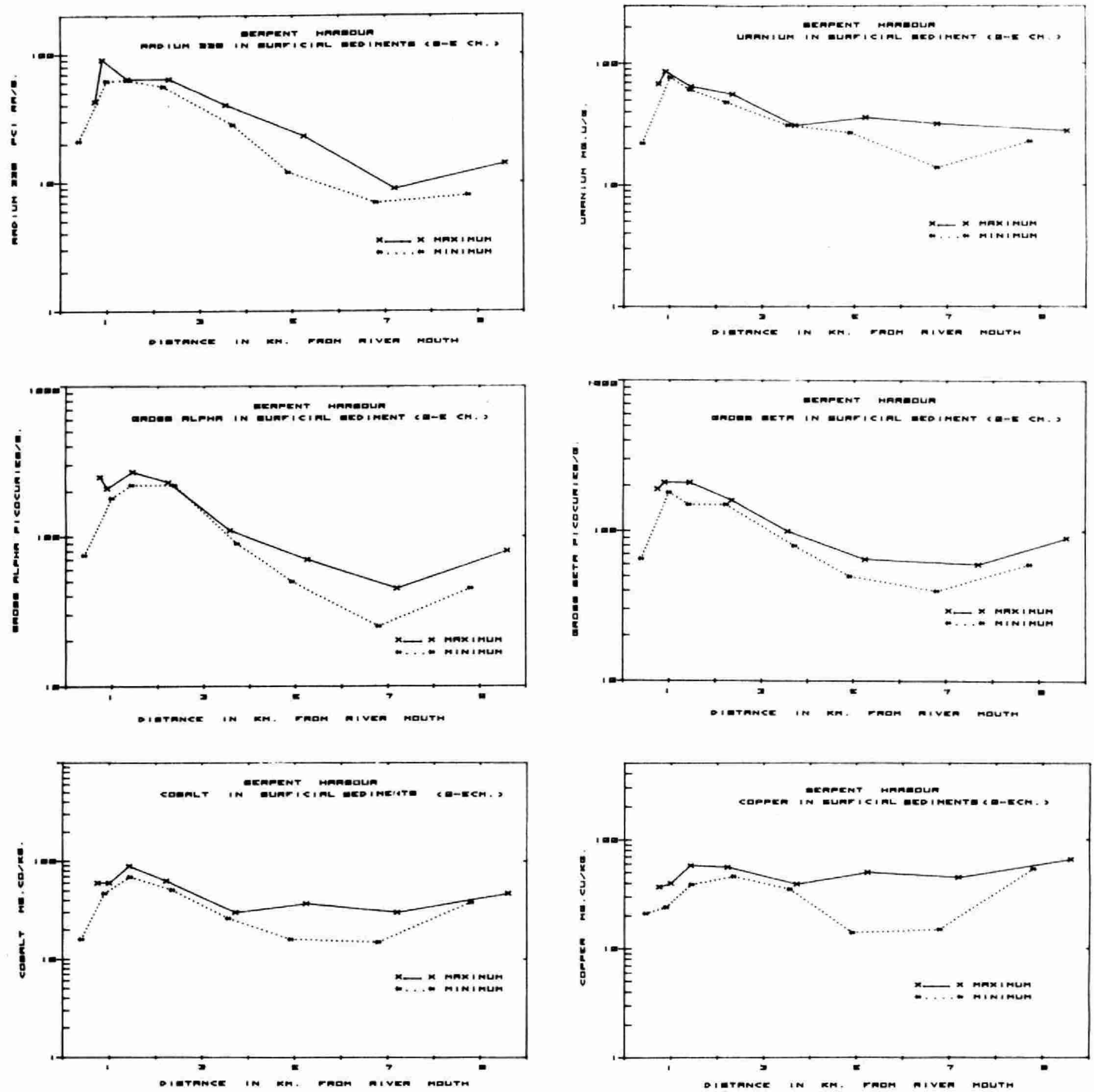

SERPENT HARBOUR
RADIUM 226 IN SURFICIAL SEDIMENTS (B-E CH.)
RADIUM 226 PCI RA/G.
X——X MAXIMUM
.... MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
URANIUM IN SURFICIAL SEDIMENT (B-E CH.)
URANIUM MG.U/G.
X——X MAXIMUM
.... MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
GROSS ALPHA IN SURFICIAL SEDIMENT (B-E CH.)
GROSS ALPHA PICOCURIES/G.
X——X MAXIMUM
.... MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
GROSS BETA IN SURFICIAL SEDIMENT (B-E CH.)
GROSS BETA PICOCURIES/G.
X——X MAXIMUM
.... MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
COBALT IN SURFICIAL SEDIMENTS (B-ECH.)
COBALT MG.CO/KG.
X——X MAXIMUM
.... MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
COPPER IN SURFICIAL SEDIMENTS (B-ECH.)
COPPER MG.CU/KG.
X——X MAXIMUM
.... MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH

FIGURE 18

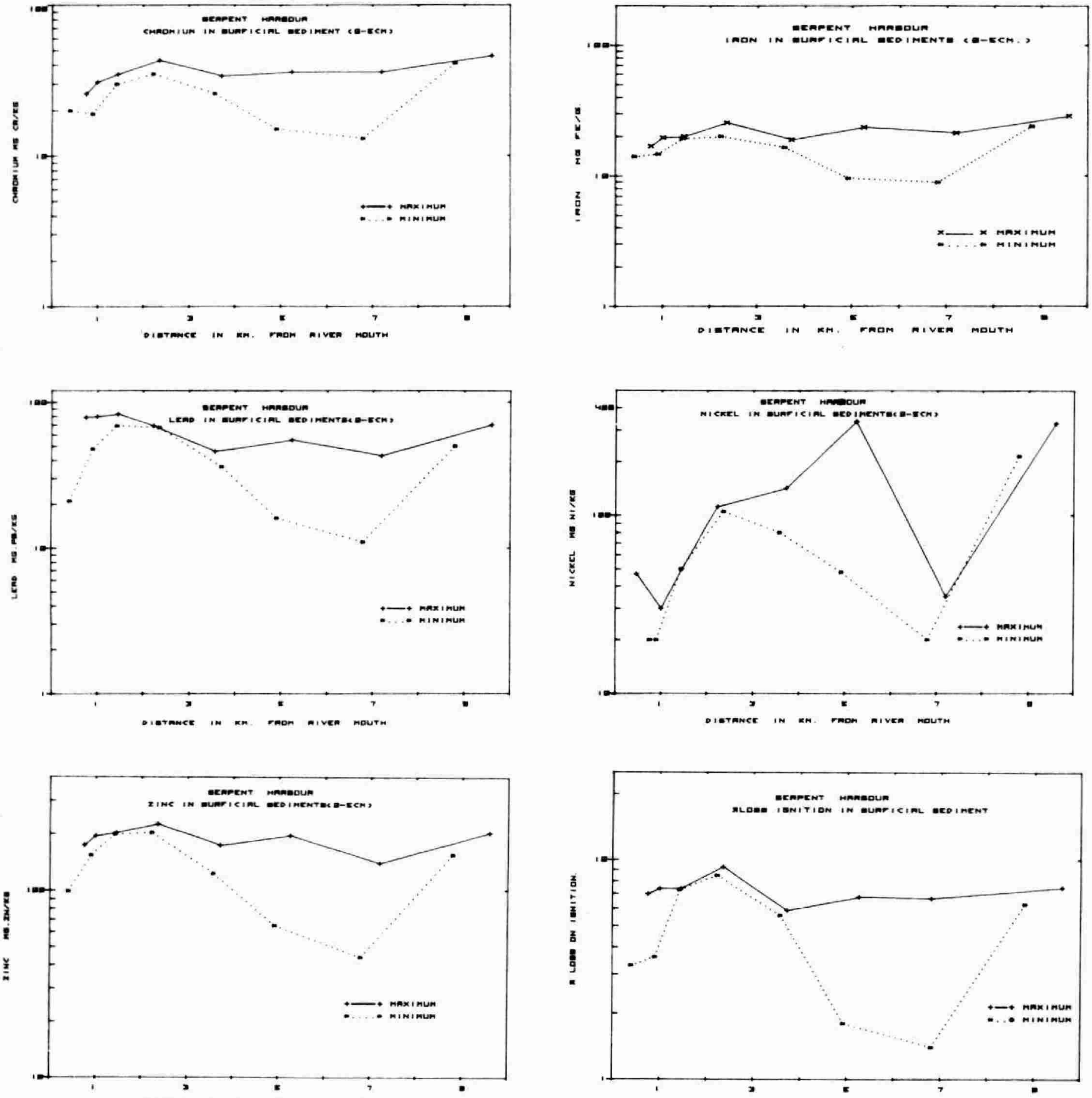

SERPENT HARBOUR
CHROMIUM IN SURFICIAL SEDIMENT (S-ECH)
MAXIMUM
MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
IRON IN SURFICIAL SEDIMENTS (S-ECH.)
MAXIMUM
MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
LEAD IN SURFICIAL SEDIMENTS(S-ECH)
MAXIMUM
MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
NICKEL IN SURFICIAL SEDIMENTS(S-ECH)
MAXIMUM
MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
ZINC IN SURFICIAL SEDIMENTS(S-ECH)
MAXIMUM
MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH
SERPENT HARBOUR
%LOSS IGNITION IN SURFICIAL SEDIMENT
MAXIMUM
MINIMUM
DISTANCE IN KM. FROM RIVER MOUTH

FIGURE 19

TABLE 9

SERPENT HARBOUR

HEAVY METALS IN SURFICIAL SEDIMENTS

MAY 30, 1975

METAL	ANALYTICAL METHOD	GEOMETRIC MEAN	SAMPLE SIZE	+S.D.	-S.D.	MIN.	MAX.
Mercury (mg/kg)	Flameless A.A.S.	.05	2	.08	.04	.04	.07
Chromium (mg/kg)	A.A.S.	28	20	40	20	13	46
Cadmium (mg/kg)	A.A.S.	1.2	20	1.5	1.0	<1.0	1.5
Lead (mg/kg)	A.A.S.	46	20	81	27	11	83
Zinc (mg/kg)	A.A.S.	145	20	223	94	44	226
Nickel (mg/kg)	A.A.S.	72	20	172	30	20	335
Cobalt (mg/kg)	A.A.S.	35	20	60	21	16	89
Copper (mg/kg)	A.A.S.	37	20	58	24	14	68
Iron (mg/g)	A.A.S.	20.3	20	38.8	10.6	9.6	28.8

<u>Note</u>:
- All data for recent surficial (0-5 cm) sediments in harbour encompassing an area of 4.14 km^2.
- All samples composited from similar duplicate Ponar grab samples.
- Harbour sediments of uniform composition-fine dark grey silt.
- All metals analyzed by OMOE Main Laboratory, Rexdale, Ontario.
- A.A.S.-Atomic Absorption Spectrophotometry.

TABLE 10

NORTH CHANNEL SEDIMENTS

Multiple Linear Correlation Matrix
based on 19 surficial (0-5cm) "Shipek"
grab samples

	Zn	Cd	Pb	Cu	Cr	Ni	Fe
Cd	.90						
Pb	.97	.88					
Cu	.42	.54	.52				
Cr	.91	.91	.90	.53			
Ni	.78	.74	.74	.35	.63		
Fe	.87	.89	.84	.44	.95	.60	
O.M.	.90	.88	.90	.51	.96	.61	.89

SERPENT HARBOUR SEDIMENTS

Multiple Linear Correlation Matrix
based on 20 surficial (0-5cm)
"Ponar" grab samples

	Zn	Cd	Pb	Cu	Cr	Ni	Fe	O.M.	Co	α	β	^{226}Ra
Cd	.72											
Pb	.90	.67										
Cu	.74	.81	.72									
Cr	.78	.80	.65	.85								
Ni	.35	.60	.14	.56	.69							
Fe	.83	.84	.69	.87	.98	.70						
O.M.	.61	.49	.71	.65	.69	.19	.66					
Co	.70	.52	.81	.42	.37	-.06	.39	.46				
α	.64	.22	.70	.19	.10	-.40	.19	.30	.71			
β	.67	.16	.74	.25	.22	-.34	.26	.33	.68	.98		
^{226}Ra	.60	.19	.62	.18	.08	-.44	.16	.28	.63	.96	.93	
^{238}U	.57	.20	.65	.12	.01	-.38	.12	.17	.59	.94	.94	.91

NOTE:
- all harbour samples of uniform composition - fine dark-grey silt
- all samples composited from two similar "Ponar" or "Shipek" casts. Surface sample only (0-5cm).

TABLE 11 HEAVY METALS IN SURFICIAL SEDIMENTS ALONG THE NORTHSHORE OF THE NORTH CHANNEL

Metal (units)	Geometric Mean	Sample Size	+S.D. (16)	-S.D. (16)	Min.	Max.
Mercury (mg/kg)	.030	19	.085	.010	<.01	.149
Chromium (mg/kg)	31.1	19	65.7	14.7	9.3	68.9
Cadmium (mg/kg)	2.5	19	3.2	1.9	<2.0	3.91
Lead (mg/kg)	26.0	19	52.7	12.8	9.0	99.2
Zinc (mg/kg)	75.1	19	170.0	33.3	17.8	233
Nickel (mg/kg)	54.9	19	169.1	17.9	19.8	562
Copper (mg/kg)	26.3	19	94.1	7.4	3.0	489
Iron (mg/g)	18.1	19	32.9	10.0	5.7	48.5

NOTE:
- Samples composited from a minimum of two similar Shipek™ casts (0-5cm)
- Samples at variable composition
- Total metals analysis performed by OMOE Main Laboratory, Rexdale, Ontario, using atomic absorpition spectrophotometry.

along the southern edge of the harbour; and 2) the pathway for minimum cross-sectional concentrations which predominated at stations along the northern edge of the harbour. Figures 18 and 19 show the lakeward gradients for minimum and maximum sediment contaminant concentrations for these cross-sections. In most cases, large differences are noted between minimum and maximum gradients which highlights the process of differential sedimentation within the harbour, e.g. Figure 19 zinc distribution.

^{226}Ra in Sediment

The frequency distribution of ^{226}Ra in the surficial (0-5 cm) sediments of Serpent Harbour was log normal with a range of levels from 7 to 91 pCi/g(dry) (Table 7). The horizontal distribution of radium was source related to the discharge of the Serpent River, with a diminishing lakeward gradient of levels (Figure 18) and maximum accumulations along the southern edge of the harbour. The vertical distibution of radium in core samples (Table 8) suggested that radium accumulation in sediment is probably of recent origin with maximum levels noted in the surficial portion of the core (0-5 cm). Statistically significant linear correlations (table 10) were noted for ^{226}Ra versus gross α, gross β, U^{238} cobalt, zinc and lead. The correlation with gross α, gross β, and U^{238} is to be expected as well as the correlation with lead, the long term decay product of the uranium series. A plausible explanation for the radium versus zinc and radium versus cobalt correlations was not apparent.

A few general approximations can be given to suggest the nature of ^{226}Ra sedimentation within the harbour; 1) the suspended solid load of the Serpent River is of small particle size range as indicated by the composition of harbour sediments with consist of fine silt-size fractions; 2) the chemical similarity of radium to calcium; 3) the influence of neutral to slightly acid pH on the solubility of radium and its salts; and 4) the uptake of ^{226}Ra by plankton and the rain of detritus to the bottom is probably the major pathway for radium accumulation in sediment. Some general estimates are provided in the literature for vertical diffusion rates of radium in oceanic sediments (16); however little is reported about ^{226}Ra vertical diffusion rates in shallow Precambrian freshwater sediments.

Other Radiochemical Distributions in Sediment

The frequency distribution of U^{238} in the surficial (0-5 cm) sediments of Serpent Harbour was log normal with a range in concentration from 14 to 86 μg/g(dry) (table 7). The horizontal distribution of uranium was source related to the discharge to the Serpent River with a diminishing lakeward gradient of levels (figure 18) and maximum accumulations along the southern edge of the harbour.

Similar horizontal distributions were noted for gross α, gross β and cobalt in the surficial sediments of the harbour

(Figure 18) and supported by statistically significant linear correlations between variables (Table 10). The vertical distribution of gross α, gross β and U^{238} in sediment cores (Table 8) indicated recent accumulations with maximum levels noted in surficial sub-samples (0-5 cm). Gradients of vertical distributions were not as dramatic as noted for ^{226}Ra suggesting that subsurface accumulations (5 to 20 cm) are the result of natural accumulation over a longer period. Gross α and gross β activity in sediment cores is greater than can be accounted for by ^{226}Ra and U^{238} alone, as such, it is probable that other daughter products of the uranium series are present.

Heavy Metals in Sediment

For the present study, surficial sediments were analysed using atomic absorption spectrophotometry (6) for the determination of total metals including: mercury, chromium, cadmium, lead, zinc, nickel, cobalt, copper and iron (table 9, figure 19). Frequency distributions of nickel and cobalt were positively skewed log-normal. Zinc and lead were negatively skewed log-normal; and copper and chromium normally distributed. The majority of metals, with the exception of nickel showed similar lakeward concentration gradients (figure 19) with maximum cross-sectional concentrations along the south shore of the harbour. All metals with the exception of nickel and zinc were less than 100 mg/kg. Mercury was found in low background concentrations (.05 mgHg/kg).

For comparative purposes, North Channel metal concentrations in surficial sediments (table 11) and multiple linear correlations between variables (table 10) are included. Except for lead, nickel and zinc, sediment metal levels in the harbour were within the range noted for sediments of the north shore of the North Channel.

The horizontal distribution of nickel in the surficial sediments of Serpent Harbour was distinctly different relative to all other metal distributions. A wide range in nickel levels from 20-335 mgNi/kg was noted (figure 19), table 9). Negative linear correlations were noted for several sediment variables as well as signficant positive correlations of nickel with iron, cadmium and chromium (table 10). Explanation of the distribution of nickel, zinc and lead and possible sources are not forwarded at this time.

Pesticides and PCB's in Sediment

The sediments of Serpent Harbour were devoid of detectable quantities of lindane, heptachlor, aldrin, dieldrin, endrin, heptachlor epoxide, DDT, PCB's and chlordane (table 12). Minute traces of DDE (geometric mean 1.2 μg/kg) were noted in surficial sediments at 14 stations, as well as DDT which was detected at 2 stations with levels of 2 μg/kg (table 12).

TABLE 12

SERPENT HARBOUR

ORGANOCHLORINE AND PCB IN SURFICIAL SEDIMENTS μg/kg

MAY 30, 1975

COMPOUND	GEOMETRIC MEAN	SAMPLE SIZE	+.S.D.	-S.D.	MIN.	MAX.
Lindane	N.D.	20				
Heptachlor	N.D.	20				
Aldrin	N.D.	20				
Dieldrin	N.D.	20				
Endrin	N.D.	20				
Heptachlor epoxide	N.D.	20				
pp' DDE	1.2	14	1.6	.9	1	2
pp' DDD	Only 2 Samples out of 20 had detectable levels of 2ppb.					
pp' DDT	N.D.	20				
op' DDT	N.D.	20				
PCB	N.D.	20				
Chlordane	N.D.	20				

<u>Note</u>: - All data for recent surficial (0-5 cm) sediments in harbour encompassing an area of 4.14 km^2.
- All samples composited from similar duplicate Ponar grab samples.
- Harbour sediments of uniform composition fine dark grey silt.
- All samples analyzed by OMOE Main Laboratory, Rexdale, Ontario using solvent extraction and gas chromatography.
- Detection limit for all compounds 1ppb. (1 μg/kg), except for PCB 10ppb. (10 μg/kg).

N.D. - None detected.

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